

High-resolution compound-specific mapping in works of art via data fusion of MA-XRPD with hyperspectral data (part 1: Method evaluation)

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ABSTRACT

Background: Hyperspectral imaging techniques have emerged as powerful tools for non-invasive investigation of artworks. This paper employs either reflectance imaging spectroscopy (RIS) or macroscopic X-ray fluorescence (MA-XRF) imaging in combination with macroscopic X-ray powder diffraction (MA-XRPD) for state-of-the-art chemical imaging of painted cultural heritage artefacts. While RIS can provide molecular information and MA-XRF can offer elemental distribution maps of paintings of high lateral resolution, the unique advantage of MA-XRPD lies in its ability to visualize the distributions of specific pigments and estimate in a quantitative manner the relative concentrations of the crystalline phases at the surface of artworks. However, MA-XRPD is more time-consuming and offers a lower lateral resolution than RIS and MA-XRF.

Results: This study introduces a machine learning (ML) approach to obtain the distribution of specific compounds on the surface of artworks with a resolution that is comparable to that of RIS and MA-XRF data but with the compound specificity of MA-XRPD. The general aim is to expedite non-destructive artwork imaging analysis by fusing data from different imaging modalities via machine learning models. The effect of preprocessing techniques to enhance the predictive accuracy of the models is explored. The paper demonstrates the method's efficacy on a 16th-century illuminated manuscript, showcasing the feasibility of predicting compound-specific distribution maps. Three evaluation methods—visual examination of the predicted distribution, root mean square errors (RMSE), and feature permutation importance (FPI)—are employed to assess model performance. Fusing MA-XRF with MA-XRPD led to the best RMSE scores overall. However, fusing the RIS and MA-XRPD data blocks also yield very satisfactory and easily interpretable high-resolution compound maps.

Significance: While MA-XRPD allows for highly specific imaging of artworks, its time-consuming nature and limited resolution presents a bottleneck during non-invasive imaging of painted works of art. By integrating data from more time-efficient hyperspectral techniques such as MA-XRF and RIS, and employing machine learning, we expedite the process without compromising accuracy. The fusion process can also denoise the distribution maps, improving their readability for heritage professionals and art historical scholars.

1. Introduction

Hyperspectral imaging techniques have emerged as powerful tools for non-invasive investigation of works of art. These methods provide valuable information about the heterogeneous composition within entire artworks, aiding in the identification of the pigmented materials

that were employed, yielding a better understanding of the techniques employed by the artists, and sometimes revealing hidden features in the works of art [1–4].

Among these techniques, reflectance imaging spectroscopy (RIS) has come forward as a time-efficient method that provides essential information about the underlying structures in artworks [5]. RIS operates by

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capturing reflectance spectra across a range of wavelengths, allowing to analyze electronic transitions in the visible and near-infrared (VNIR) range as well as vibrational modes in the short-wavelength infrared (SWIR) range. While RIS provides valuable molecular information, it has some limitations in terms of the spectral data it offers. Specifically, reflectance spectra within the VNIR range may lack the level of detail and fingerprinting capabilities encountered in other molecular spectroscopic techniques such as FT-IR or Raman spectroscopy. This can pose challenges to identify and estimate the relative abundance of artists' materials, especially when dealing with mixtures of compounds that exhibit overlapping spectra. Hence, RIS is often combined with other hyperspectral imaging methods such as Macroscopic X-ray Fluorescence (MA-XRF) Imaging [6–8]. Furthermore, this multimodal analytical approach is commonly supported by machine learning methods, which have gained significant traction in recent years in the field of cultural heritage [9–11]. Machine learning is proving invaluable not only for the interpretation of multimodal data but also for improving the analysis of single-modality studies by providing advanced data interpretation and pattern recognition capabilities [12–18].

In the last decade, MA-XRF has become a widely used for the analysis of artworks; it detects the characteristic X-ray fluorescence emitted by the chemical elements present within an artwork. This enables the (indirect) identification of pigments used by an artist and the uncovering of modifications that may have occurred during the creation of the artwork or during restoration procedures [19,20]. However, direct compound identification can be challenging, especially in cases where multiple pigments share similar elemental compositions. For example the artists' pigments lead white (cerussite, PbCO_3 and/or hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), red lead (minium, Pb_3O_4) and massicot (o-PbO) are differently colored compounds that all will contribute to the elemental Pb-L and Pb-M distribution maps obtained by MA-XRF while quite a few of the other elements present in these materials (such as O, C, Si) are not detectable because of their too low characteristic XRF energies and thus cannot be used to differentiate between the various pigments.

In contrast, Macroscopic X-ray Powder Diffraction (MA-XRPD) imaging stands out for its ability to provide highly specific and quantitative spectral information about crystalline materials [21]. For example, Vanmeert et al. were able to identify and map four different lead-based compounds in a 15th/16th century illuminated manuscript [8]. Next to visualization of the distribution of crystalline compounds, MA-XRPD also allows for detailed phase identification and provides information on the relative abundance of these crystalline species; for example, different subtypes of the pigment lead white may be distinguished from each other based on the mass ratio between its two components hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) and cerussite (PbCO_3) [22,23]. However, the advantages associated with the high specificity of MA-XRPD come at a cost: MA-XRPD scanning requires considerable longer data collection times per pixel than the aforementioned hyperspectral techniques, making it time-consuming to analyze large areas of artworks. In addition, the lateral resolution of “as collected” MA-XRPD maps is inferior to that of the distributions typically produced by RIS or MA-XRF scanning. To address the trade-offs between time efficiency and spectral specificity offered by the different hyperspectral imaging techniques, we propose employing machine learning (ML) methods to fuse MA-XRPD data with data imagery obtained by complementary hyperspectral methods such as MA-XRF and RIS.

In the presented study we aim to combine the high spatial resolution characteristics of RIS or MA-XRF with the high species-specificity of MA-XRPD by employing random forest regression models, thereby facilitating the generation of compound distribution maps with high spatial resolution. The primary objective of this paper therefore is to develop and evaluate a reliable and efficient ML-based approach for predicting the abundance maps of several crystalline compounds, obtained by scanning the vegetal borders of a 16th century illuminated manuscript shown in Fig. SI-1A. We focus our attention on this type of painted artefacts because of their straightforward stratigraphic buildup (often only

one pigmented layer is used) while also a smaller range of colored paint compounds is employed than in oil paintings. Additionally, we explore the impact of various data preprocessing methods on prediction performance. Finally, to demonstrate the applicability of the method to more complex painted works of art, we use random forest regression models to predict compound distribution maps with enhanced spatial resolution based on MA-XRF and MA-XRPD distribution maps collected from a flower piece painting (Fig. SI-1B) described in detail elsewhere [24].

The added value of this ML-based fusion procedure can be perceived in a different manner depending on the primary interest of scientists or heritage scholars that are involved. From the point of view of analysts/method developers that are primarily interested in optimizing the MA-XRPD method of analysis, the main advantage of the multi-modal fusion is that it allows to reduce the negative impact of two important limitations of MA-XRPD (i.e., very long acquisition times and coarse-grained images) while retaining most of its strong points (i.e. high compound-specificity, quantitative nature). On the other hand, many heritage professionals or art scholars are primarily focused on extracting (pictorial) information from artworks via non-destructive means, regardless of the method(s) involved. For them, the main added value(s) of using a combined MA-XRF + MA-XRPD or RIS + MA-XRPD approach resides with the fact that the distribution maps typically obtained by MA-XRF or RIS can now be attributed to specific crystalline pigments/materials with a high(er) degree of confidence [8]. In a subset of cases where more than one paint component is contributing to these distributions, the fusion with MA-XRPD allows to “unmix” the MA-XRF or RIS maps, yielding high-resolution “single component” distribution images, in a similar manner as has been amply described for remote sensing/satellite imagery [25–27]. Such “pure compound” maps, that each can unambiguously be attributed to either a primary artists' material or to a degradation product of the latter, represent highly valuable and reliable input for studies in art history [23], heritage science [24] or art conservation [21].

2. Experimental methods

2.1. Measurements

Various non-destructive imaging methods were employed to collect hyperspectral data blocks from two painted works of art showing a representative variety of pigments and related artists' materials: (a) a (genuine) 16th c. illuminated manuscript (Fig. 2) and (b) a (fake, Dutch 17th c. style) oil painting of a flower arrangement (Fig. 5).

2.1.1. MA-XRPD

MA-XRPD measurements were performed on both the manuscript and the painting using an in-house built MA-XRPD instrument which employs a 50 W Cu-anode X-ray micro source. These measurements were conducted in transmission for the illuminated manuscript and in reflection mode for flower piece painting. Diffraction patterns were collected using a PILATUS 200 K detector. Processing of the diffraction data was performed using the XRDUA software following a procedure that has been described elsewhere [21].

From the illuminated manuscript, 8 meaningful compound-specific distribution images could be obtained: azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), posnjakite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), metallic gold (Au^0), calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), lead tin yellow (Pb_2SnO_4), hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$).

From the flower piece painting, executed in the style of 17th C. Dutch painter but painted with 20th c. pigments, meaningful MA-XRPD distributions of 8 crystalline pigments could be obtained: cadmium red ($\text{CdS}_{1-x}\text{Se}_x$, with $x \approx 0.5$), chrome yellow (PbCrO_4 , crocoite), titanium white (TiO_2 , rutile), chalk (CaCO_3 , calcite), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), yellow ochre (FeOOH , goethite), prussian blue ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$) and ultramarine blue ($(\text{Na,Ca})_8(\text{AlSiO}_6)_6$, lazurite) (Fig. SI-1B).

2.1.2. MA-XRF

To unravel the elemental composition of both the manuscript (Fig. SI-1A) and the oil painting (Fig. SI-1B), we employed an in-house built MA-XRF scanner (ATLAS). This advanced device utilizes a 50-W Rh-anode X-ray tube in conjunction with four Vortex EX-90 SDD detectors to capture elemental spectra.

For the manuscript, a comprehensive MA-XRF scan was conducted in reflection mode over a duration of 1.2 h. This process yielded detailed elemental maps encompassing key elements such as P, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Au, Pb, and Sn.

For the oil painting, similar settings were employed using a dwell time of 30 ms/pixel and a step size of 0.5 mm, resulting in a scan time of 4.5 h and meaningful MA-XRF maps of S, Ca, Ti, Cr, Fe, Pb, Se and Cd (Fig. SI-1B).

2.1.3. RIS

Reflectance Imaging Spectroscopy (RIS) was employed to capture spectral reflectance data spanning the Visible and Near-Infrared (VNIR) and Short-Wave Infrared (SWIR) regions. Three specialized hyperspectral cameras facilitated high-resolution imaging, resulting in three RIS datasets: VNIR (400–1000 nm), short SWIR (900–1700 nm), and long SWIR (900–2500 nm). VNIR data acquisition lasted 1.67 min at 0.168 mm spatial resolution. Short SWIR scanning required approximately 25 s at a 0.17 mm resolution. Long SWIR imaging, at a 0.168 mm resolution, took around 5 min.

2.2. Model architecture

First, the MA-XRPD, MA-XRF and RIS datasets were registered to one another by using a grayscale image as reference. For this, common features were searched for by SIFT (Scale-Invariant Feature Transform) in monochromatic representations of the datasets and the grayscale image by using the DataHandlerP software [28]. The dimensions of all datasets were adjusted to the dimensions of the dataset with the lowest resolution, which is the MA-XRPD dataset. The procedure for creating the prediction models is shown in Fig. 1; each step is explained in more detail below. Then various preprocessing methods were applied to both MA-XRF and RIS datasets to test their influence on the regression models. For MA-XRF, linear, log-transformed, and log-log-transformed data was included, as well as elemental distributions obtained by fitting a spectral model to the linear data. RIS datasets comprised linear (smoothed), standard normal variate (SNV) transformed, and first derivative data.

For each of the eight crystalline compounds considered in this study,

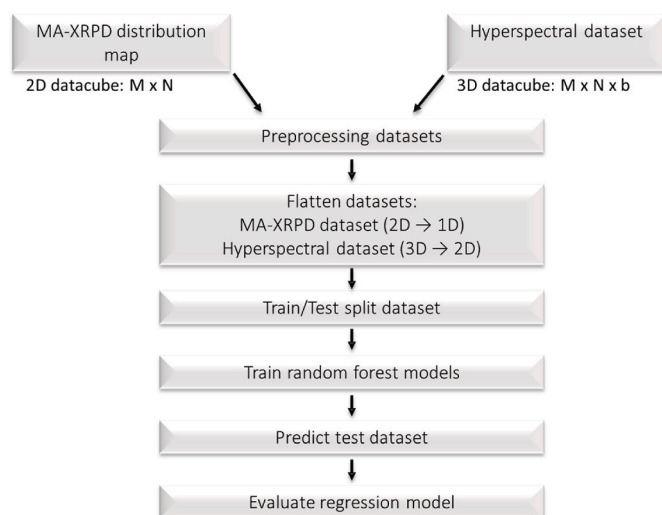


Fig. 1. Schematic overview of workflow for model architecture.

the following steps were repeated separately. Thus, a total of eight models was created for each dataset, corresponding to the compounds: azurite, malachite, posnjakite, gold, calcite, gypsum, lead tin yellow and hydrocerussite.

For each particular compound, the MA-XRPD based relative abundance data is loaded into a 2D matrix (MxN), where M and N are the number of pixels in the x- and y-direction and used as the ground truth or reference values. The corresponding hyperspectral dataset (MA-XRF or RIS) is loaded into a 3D matrix (MxNxb), where b is the number of spectral bands. The next step is to combine the MA-XRPD set with the hyperspectral set. The first two dimensions of the two matrices are flattened into a vector of length $L = M \times N$. This flattening is necessary to use the machine learning algorithm. This results in a 1D vector (of dimension L) containing the MA-XRPD data and a 2D matrix (of dimensions Lxb) with the hyperspectral data. So, for each pixel in the map (characterized by a MA-XRF or RIS spectrum of length b) there is a corresponding abundance value as determined by MA-XRPD for the specific crystalline compound under consideration. The resulting dataset is then split into a training and testing set with a ratio of 30/70. The size of the training set is deliberately set to only 30 % to prevent overfitting the model. A random forest regression model is trained on this data [29]. The random forest algorithm uses multiple parallel decision trees whose results are averaged to achieve a higher overall prediction accuracy. A random subset of the training dataset is used to create each decision tree. Averaging or ensemble methods are commonly used in machine learning to achieve higher accuracy compared to non-ensemble methods [30]. As with most machine learning algorithms, there are a number of hyperparameters that can be defined and fine-tuned. A parameter optimization algorithm is used to determine the most successful set of hyperparameters for the model [31]. Five-fold cross-validation is used to calculate the mean accuracy of the model. After tuning the algorithm, we can use the best parameters to predict a high-resolution compound abundance map based on the corresponding hyperspectral dataset. The training subset of pixels in the dataset is omitted when calculating the correlation metrics between ground truth data (based on low resolution MA-XRPD measurements) and the predicted high-resolution compound abundance response. The correlation metrics used are explained in more detail in section 2.5. The open source Python package “sci-kit learn” was used to implement these algorithms [32].

2.3. Model validation

2.3.1. Root mean square error (RMSE)

The Root Mean Square Error (RMSE) is a measure for estimating the difference on a pixel-by-pixel level between two images A and B. RMSE is an often-used similarity comparison metric, however if the values of the pixels in images A and B are slightly shifted, this will have a strong impact on the RMSE value even though both images will still have a similar appearance. The RMSE is calculated using equation (1):

$$RMSE_j = \sqrt{\frac{1}{K} \sum_{i=1}^K (\hat{y}_{ij} - y_{ij})^2} \quad (1)$$

with K as the total number of pixels, $\hat{y}_i$ is the predicted abundance of compound j at image pixel i and y_{ij} the experimentally determined MA-XRPD abundance of compound j at this pixel. As mentioned above, the data is split in a training and a testing set. For each compound considered, a different test set is created using the following strategy: the set of abundance values of this compound in all pixels are sorted and split up in ten histogram bins so that the entire concentration range is equally divided, and 150 pixels in each bin are randomly selected for the testing set. In this manner the testing set will validate the entire abundance range without having a bias towards the abundance levels that appear most frequently.

2.3.2. Feature permutation importance (FPI)

Feature permutation importance (FPI) is a model inspection technique that is particularly useful for non-linear data [33]. FPI involves the perturbing or repositioning of a single feature (i.e., the detected spectral intensity at a specific wavelength/energy) within the dataset and then observing how this alteration impacts the performance of the model. This means that the recorded values of that particular feature are set to a random value while keeping the values of all other features (i.e., the spectral intensity at all other wavelengths/energies in the spectrum) and the corresponding ground truth data unchanged. By measuring the resulting decrease in the predictive accuracy of the model, it is possible to obtain a quantitative measure of the level of importance that each feature has on the overall prediction accuracy of the model. In essence, this approach sheds light on the extent to which the model relies on each

spectral wavelength/energy for making accurate predictions. However, it is essential to note that when two or more features are correlated, permuting one feature may still allow the model to access the information through its correlated features. This can lead to lower importance values for both features, where they might actually be important. Hyperspectral datasets are highly correlated datasets. To address the correlation and obtain meaningful insights from the analysis, a strategy is employed where instead of a single feature being perturbed, multiple hyperspectral features are perturbed for the importance calculation of a specific spectral feature. The number of features being shuffled is tailored to the specific spectral characteristics of the hyperspectral dataset, allowing us to gain a clearer understanding of the importance of individual spectral features.

For detailed information regarding the investigated artworks,

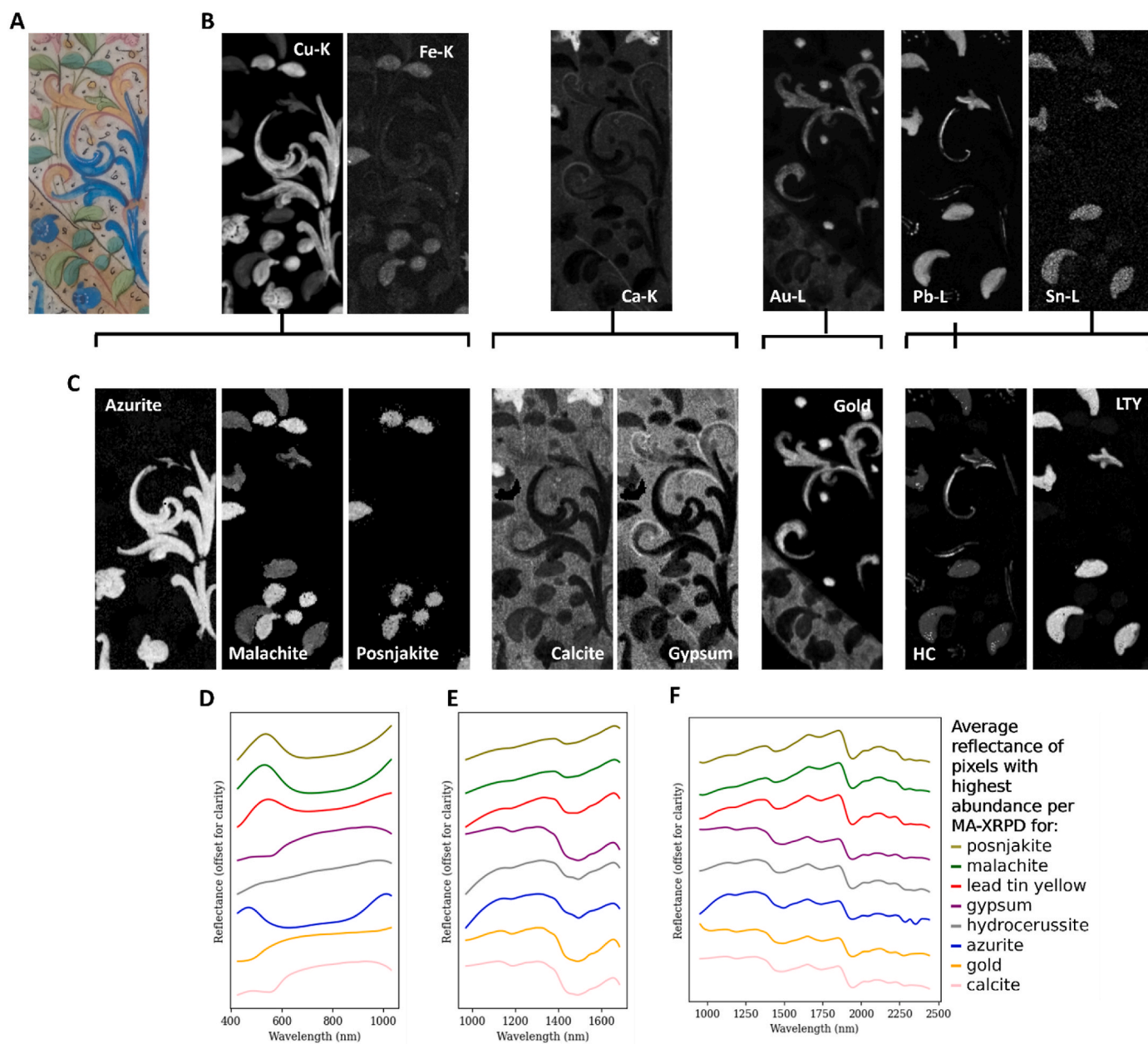


Fig. 2. (A) Photograph of the scanned region for the front side of the illuminated manuscript together with corresponding (B) element-specific MA-XRF and (C) phase-specific MA-XRPD abundance distributions. Lighter tones indicate a higher XRF intensity or XRPD abundance, corresponding respectively to a higher elemental or compound abundance in each pixel. Compounds imaged: azurite - $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; malachite - $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; posnjakite - $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$; calcite - CaCO_3 ; gypsum - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; gold - Au^0 ; hydrocerussite - $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$; lead tin yellow - Pb_2SnO_4 . (D–F) Average reflectance spectra of pixels showing the highest abundance for the specified crystalline phases in the (D) VNIR, (E) short SWIR and (F) long SWIR spectral range.

instrumentation specifications and preprocessing methods please refer to the Supplementary Information.

3. Results & discussion

Before employing ML techniques, understanding the dataset is crucial. Subsection 3.1 describes the materials employed in the illuminated manuscript, thereby facilitating a better understanding of both the artwork and the ML algorithm. This section is followed by the validation methods for the model, starting with a visual comparison between ground truth MA-XRPD abundance maps and model predictions. Then in subsection 3.3, to compare the accuracy of the various models, the Root Mean Square Error (RMSE) is calculated between ground truth and predicted maps. Finally, Feature Permutation Importance (FPI) analysis highlights the significance of the spectral feature in achieving predictive accuracy in subsection 3.4.

3.1. Exploration of the manuscript datasets

In Fig. 2 the element-specific MA-XRF and phase-specific MA-XRPD abundance maps are shown as experimentally recorded, alongside the average RIS spectra of pixel clusters utilizing the top 20 % of relative abundance obtained through XRD for each compound. Fig. 2E and F shows strikingly similar spectra in the SWIR range, possibly due to deeper SWIR radiation penetration into paint layers, highlighting features primarily from the parchment at wavelengths around 1201, 1500 (broad), 1730, 1940, 2040, and 2178 nm.

A strong Ca-K XRF signal was noted throughout most of the manuscript; as visualized with MA-XRPD, this corresponds to the presence of calcite and gypsum, which were abundantly used during the preparation of the vellum. In addition, in locations where their relative abundance is higher, these compounds are likely to have been used as inorganic substrates for one or more organic red/pink colorants (e.g., in the pink flowers). In Fig. 2D, the VNIR average spectra of the area where calcite and gypsum are present show the characteristic broad inflection point of a reddish/pinkish lake at 560 nm. While it is known that gypsum has a triple degenerated overtone related to a hydroxyl group at 1445, 1490, and 1535 nm, this triplet overtone is not found in the average gypsum spectra shown in Fig. 2E and F [2]. This could be due to the small particle size of this compound.

The MA-XRPD data shows the use of two copper carbonates, malachite and azurite throughout the decorations; the more rare copper sulphate mineral posnjakite is also present, previously identified in late 15th and 16th century artworks [34]. The Cu-K MA-XRF map shows a summed combination of the distribution of all three copper containing compounds. In the VNIR range (Fig. 2D), azurite features a maximum reflectance peak at 465 nm with an absorbance centered at 700 nm and a consequent rise in reflectance. SWIR spectra feature azurite's characteristic band related to a second overtone of the stretching vibrational mode of the hydroxyl group ($2\nu\text{OH}$) at 1495 nm [35]. Furthermore, in the long SWIR data, characteristic bands around 2285 and 2350 nm are present, respectively associated with the combination band of carbonate stretching and hydroxyl bending ($\delta\text{OH} + \nu\text{CO}_3^{2-}$) and the third overtone of the carbonate stretching ($3\nu\text{CO}_3^{2-}$) of azurite [36]. As these bands are related to respectively carbonate stretching and hydroxyl bending, it is expected that malachite and hydrocerussite will show similar features. However, their exact positions can vary since the position of these bands depend on the intrinsic composition of the pigment [37–39].

In Fig. 2D, the VNIR spectrum of the pixels with highest hydrocerussite abundance, as determined by MA-XRPD, shows a typical spectrum for a white pigment, thus showing no spectral features [35]. In the SWIR range, it was expected that the presence of this compound would be visible via a characteristic band related to its hydroxyl group at 1450 nm [40,41]. However, instead the characteristic band of azurite (at 1495 nm) is visible, especially in the short SWIR (Fig. 2E). This is due to the fact that in all hydrocerussite-rich pixels of the MA-XRPD map

(Fig. 2C), also some azurite is present, either on the front or back side of the manuscript that are sampled simultaneously by MA-XRPD. It is relevant here to note a significant difference between the two RIS modalities: while VNIR samples only the top layer of the manuscript, SWIR can penetrate underlying layers. Accordingly, in the VNIR, the hydrocerussite spectrum resembles that of a (pure) white compound. However, in the SWIR, the hydrocerussite spectrum resembles that of azurite, indicating that the SWIR also captures characteristics from the underlying (blue) layers. The MA-XRPD technique allows for the identification of a second lead-containing pigment: lead tin yellow. From the correlated Sn-L and Pb-L MA-XRF distributions, an indirect identification of lead tin yellow can be made. MA-XRPD unambiguously identified lead tin yellow to be present in the manuscript, colocalized with hydrocerussite in the green leaves. Mixing lead tin yellow with malachite is known to cause a change in the green hue and therefore shows a change in the maximum reflectance peak in the VNIR spectrum [35]. The shift is also visible in Fig. 2D when comparing the VNIR spectrum of the pixels most abundant in malachite with that of the pixels most abundant in lead tin yellow. It should be noted that lead tin yellow is only found together with malachite in this parchment; thus, the average spectrum of lead tin yellow of Fig. 2D corresponds to a mixture of lead tin yellow with malachite.

Metallic gold paint is readily identified in the MA-XRPD and the MA-XRF distributions. Gold is known not to show any spectral feature in the SWIR range. The average spectrum of gold in the VNIR range shows an increase in reflectance around 490 nm and an inflection point around 510 nm, characteristic for gold [35].

3.2. Visual comparison

For four pigments, Fig. 3 compares the “ground truth” (or “as collected”) MA-XRPD maps to those predicted by the random forest models trained on MA-XRF, VNIR, and long SWIR data; see Fig. SI-2 for the predicted compound maps of gypsum, gold, posnjakite and lead tin yellow in this manuscript. It can be noted that the models are able to successfully approximate the ground truth maps, regardless of the dataset type.

For calcite, the ground truth map is noisy in the background area (where no colored compounds are present); this could be due to the intrinsic uncertainty ($\pm 5\%$) that arises from the MA-XRPD abundance determination. The predicted compound maps look less noisy as they are centered around an average background value.

Significant differences among the predicted distributions are evident in the azurite and malachite maps. On the basis of the MA-XRF data, the algorithm struggles to accurately predict where these compounds are absent/present; for example, the edges of the green leaves are predicted to contain low abundance levels of azurite while in fact this pigment is not present there (Fig. 3 and SI-3 for close-up of green leaves). Conversely, to a lesser extent the parts of the composition that contain azurite are also visible in the XRF-predicted malachite distributions. This issue arises because MA-XRF only tracks the copper abundance, present in both azurite, malachite and posnjakite, while the RIS data reflects electronic transitions, combination bands and overtones of the fundamental vibrational transitions, different for these three Cu-pigments. Thus, there is less difficulty in differentiating between these Cu-containing compounds in the corresponding RIS-based predictions. However, the XRF-based prediction of the hydrocerussite distribution is more effective compared to those based on the RIS datasets. In the VNIR- and SWIR-based predictions, hydrocerussite appears in the dark green leaves, though it is only present in the light green ones. As mentioned in subsection 3.1, hydrocerussite, being a white compound, shows no VNIR features and its characteristic spectral features were not visible in the average spectra in the SWIR range. Furthermore, hydrocerussite contains lead, which is an efficient X-ray absorber and emitter of Pb-L characteristic X-rays, resulting in more facile detection of hydrocerussite via the MA-XRF dataset.

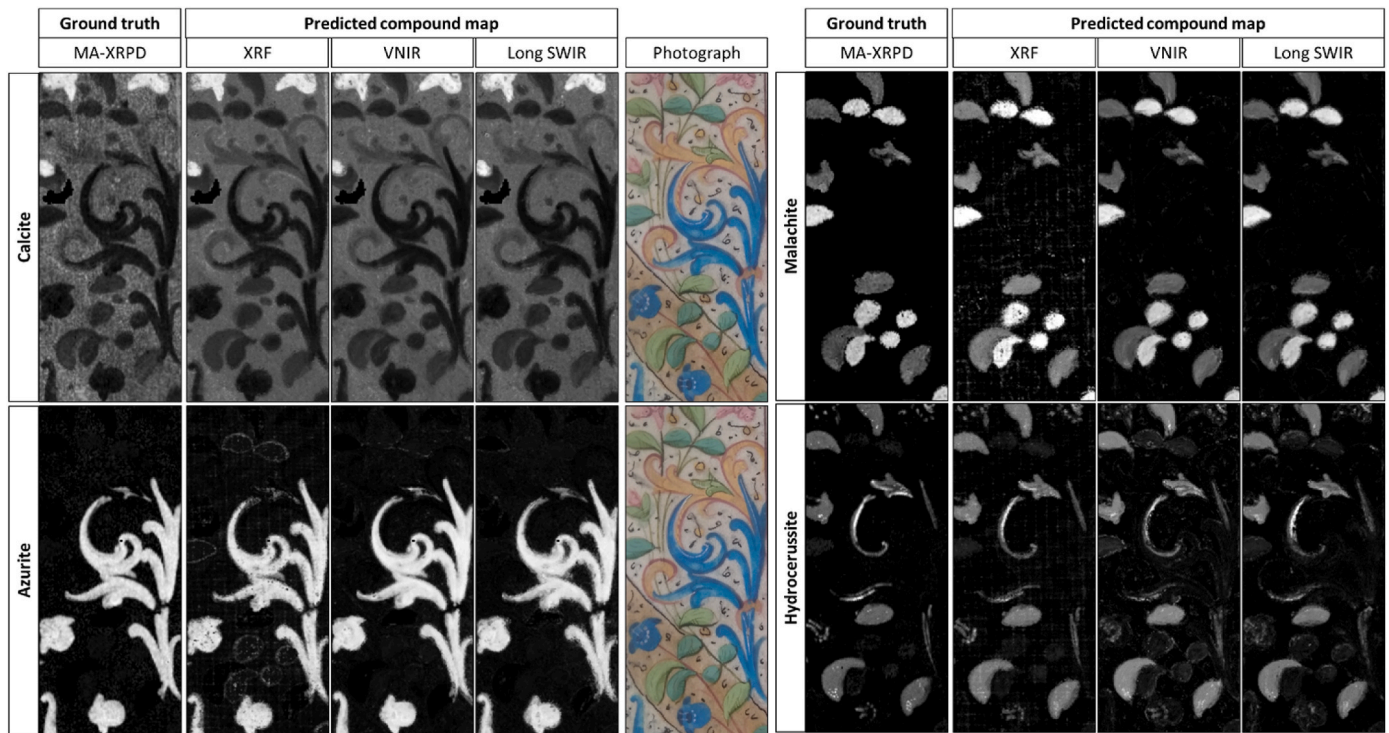


Fig. 3. Grey scale images of the ground truth, the corresponding predicted compound maps based on respectively the MA-XRF, VNIR or SWIR data cubes and a photograph of the scanned region for the front side of the illuminated manuscript.

3.3. Root mean square error (RMSE)

The RMSE obtained for all compounds using different preprocessing techniques applied to all datasets are listed in Table 1. Higher values of RMSE correspond to larger differences between the predicted and the ground truth maps. Conversely, lower RMSE values indicate smaller differences and thus a better accuracy of the prediction. Reducing the dynamic range of XRF spectra through log transformation, leads to lower RMSE values. This preprocessing step emphasizes elements with lower peak intensities, improving the accuracy of the prediction. However, further reduction via a log-log transformation increases noise and results in higher RMSE values.

The lowest RMSE values for the green compounds are obtained based on the fitted MA-XRF data, as they share similar spectra, making it challenging for models with non-fitted data to differentiate accurately. In the fitted XRF data, overlapping XRF signals are resolved and reduces noise, particularly for elements with spectral overlap such as Sn-L (overlap with K-K).

It should also be noted that the reduction in dimensionality speeds up training significantly, taking only seconds compared to several minutes

for non-fitted data. However, for compounds such as calcite and gold, spectral information loss during fitting leads to a (slight) RMSE increase.

When comparing the RMSEs of the short and long SWIR models (Table 1), it was expected that by extending the SWIR spectral range from 1700 to 2500 nm, the performance of the prediction model would improve. This is confirmed: in general, lower RMSE values are obtained when the prediction is based on the long rather than the short SWIR dataset. It is known that the extended range can contain important spectral information on paint materials, which allows for example to differentiate between different carbonate-containing compounds and also between different binding media [40,42,43].

When comparing the predictive power of using the various RIS datasets, VNIR data is able to predict the abundance of all compounds most accurately (Table 1). This is likely due to the fact that the VNIR spectral range more directly reflects the color/reflectance properties of the compounds used in the illuminated manuscript, which are typically made from natural sources such as plants and minerals. The difference in sampling depth between VNIR and SWIR can also interfere with the detection of the compounds present. Only in the case of hydrocerussite, a lower RMSE value is obtained for the SWIR-based prediction. It was

Table 1
RMSE values of the different preprocessing options applied to all datasets. The lowest RMSE obtained per compound is indicated in bold.

Dataset	Preprocessing	Calcite	Gold	Azurite	Hydrocerussite	Gypsum	Lead Tin Yellow	Malachite	Posnjakite
MA-XRF	linear	7.01	6.01	17.72	6.23	7.06	8.86	9.03	8.66
	log(1+MA-XRF)	7.00	5.98	17.66	6.24	7.07	8.89	9.04	8.70
	log(log(1+MA-XRF))	7.56	6.55	18.12	6.46	7.46	10.01	9.34	9.32
	fitted XRF	8.15	6.15	17.84	5.84	7.12	7.80	7.28	7.73
VNIR	smooth	7.39	8.19	19.82	8.50	6.85	9.70	8.37	9.06
	SNV	7.28	7.89	18.84	8.27	6.83	9.58	8.12	8.90
	1Der	6.75	7.50	17.85	8.58	6.27	9.07	7.55	8.48
Short SWIR	smooth	12.49	11.72	22.32	8.28	9.13	13.61	11.74	11.34
	SNV	12.56	11.44	22.30	8.25	9.07	13.65	11.79	11.89
	1Der	13.47	12.70	22.61	9.51	9.40	14.64	12.55	12.61
Long SWIR	smooth	8.38	8.60	20.45	7.47	7.89	10.76	9.07	9.24
	SNV	8.15	8.38	19.17	7.19	7.75	10.40	8.68	8.93
	1Der	8.40	9.27	19.08	8.02	7.93	11.17	8.82	9.58

expected that SNV preprocessing of both datasets would improve the quality of the prediction because this transformation reduces the light scattering effects [44]. While the SNV transformation does not improve the prediction quality of the VNIR dataset -in most cases the RMSE values increase rather than decrease-it does improve the prediction based on the SWIR data. Taking the first derivative of RIS spectra is a common practice to enhance the detection of weaker features, particularly in regions with overlap [40,42]. Transforming VNIR data to its first derivative reduces the RMSE for most compounds, while for SWIR data, only azurite shows a significant reduction. This could be due to enhanced feature visibility at 1495 nm [43]. However, this approach may introduce artefacts or amplify noise, hindering prediction models for other compounds. Based on the RMSE values, the models made using the MA-XRF datasets yield the best predictions. It is important to keep in mind that the MA-XRF models have more difficulty in correctly predicting the Cu-based pigments such as malachite and azurite, as seen in the visual comparison shown in Fig. 3, even though this trend is not reflected in the RMSE scores. Thus, it is important to keep both the visual and statistical evaluation in mind for the assessment of the models.

3.4. Feature permutation importance (FPI)

The FPI analysis conducted on the models revealed some important insights into which parts of the MA-XRF or RIS spectra are most relevant to predict the compound distribution maps. In Fig. 4, FPI curves are shown for the average spectra of the mineral phases for calcite, azurite, lead tin yellow and malachite; the FPI data of the other mineral phases can be found in Figure SI-4.

In general, the FPI curves for the predictions based on the MA-XRF data are fairly straightforward to interpret. For the compound calcite, which contains the chemical element calcium, it can be seen in Fig. 4A that the prediction is mostly based on the spectral features situated around the Ca-K (3.8–4.1 keV) and Cu-K (8.0–8.9 keV) signals. Calcite is mostly found in the background of the manuscript, i.e., where no other compounds with strong XRF signals are present. Thus, the machine ML algorithm relates the absence of copper in the background area in an inverse manner to the presence of calcite, leading to the utilization of Cu-K lines as negative indicators. Interestingly the FPI also identifies peaks found at lower energy than the Cu-K α peak (8.04 keV) that are likely the Ca-K sum peaks (Ca-K α +Ca-K β at $3.69 + 3.69$ keV = 7.38 keV;

Ca-K α +Ca-K β at $3.69 + 4.01 = 7.7$ keV). Similarly, the XRF-based prediction of the abundance of azurite, a blue copper-containing pigment, heavily relies on the Cu-K XRF lines while the model also takes into account the Fe-K signal (at 6.4 keV) (Fig. 4B). It is well known that azurite can contain iron-containing species, such as hematite and goethite, either as impurities or in a mixture [45–47]. The prediction of the abundance of the lead-containing pigments, hydrocerussite and lead tin yellow, relies on the intensity of the Pb-L XRF lines (at 10.5 and 12.6 Kev; Fig. 4C and SI-4). Also, Sn-L lines (at 3.4 keV) play an important role in the lead tin yellow model. The prediction model for malachite makes use of the XRF Fe-K and Cu-K lines (Fig. 4D); it can be observed in Fig. 2B that the iron intensity is the highest in the malachite-rich, dark green areas. Similarly to azurite, malachite is also known to contain iron-containing impurities [47]. Additionally, in this case, the Sn-L lines are of importance since malachite was used together with lead tin yellow to obtain the lighter green tint of the leaves.

For the prediction of calcite using the VNIR dataset, the inflection point at 560 nm serves as the most important feature for accurate predictions even if it relates to the organic pink lake that is present together with calcite and not to calcite itself (Fig. 4E). The VNIR model for gold (Fig. SI-5) primarily focuses on features starting from the increase of reflectance around 480 nm, which can be attributed to the gold layer, as mentioned above. A second important region is located between 550 and 690 nm. Around 640 nm, azurite show an absorbance maximum [35]. Thus it is possible that the ML algorithm relates the absence of an absorbance around 640 nm in an inverse manner to the presence of gold. Also, the spectral features around 580–640 nm are identified as the most important for the VNIR prediction model of azurite (Fig. 4F). Both for malachite and posnjakite, in the wavelength range from 500 to 600 nm, a maximum can be observed in the FPI and the average reflectance spectrum. The range of 480–600 nm is also identified as the most important wavelength range for the models of lead tin yellow (Fig. 4G), malachite (Fig. 4H), posnjakite (SI) and hydrocerussite (SI). This can be explained by the fact that lead tin yellow, hydrocerussite, malachite and posnjakite can all be found in the green colored leaves. The end of the VNIR spectrum is also identified as an important region for malachite and posnjakite.

In the analysis of both SWIR datasets, it became apparent that most of the important features for all the models were identified as bands related to the support layer of the manuscript or the vellum itself

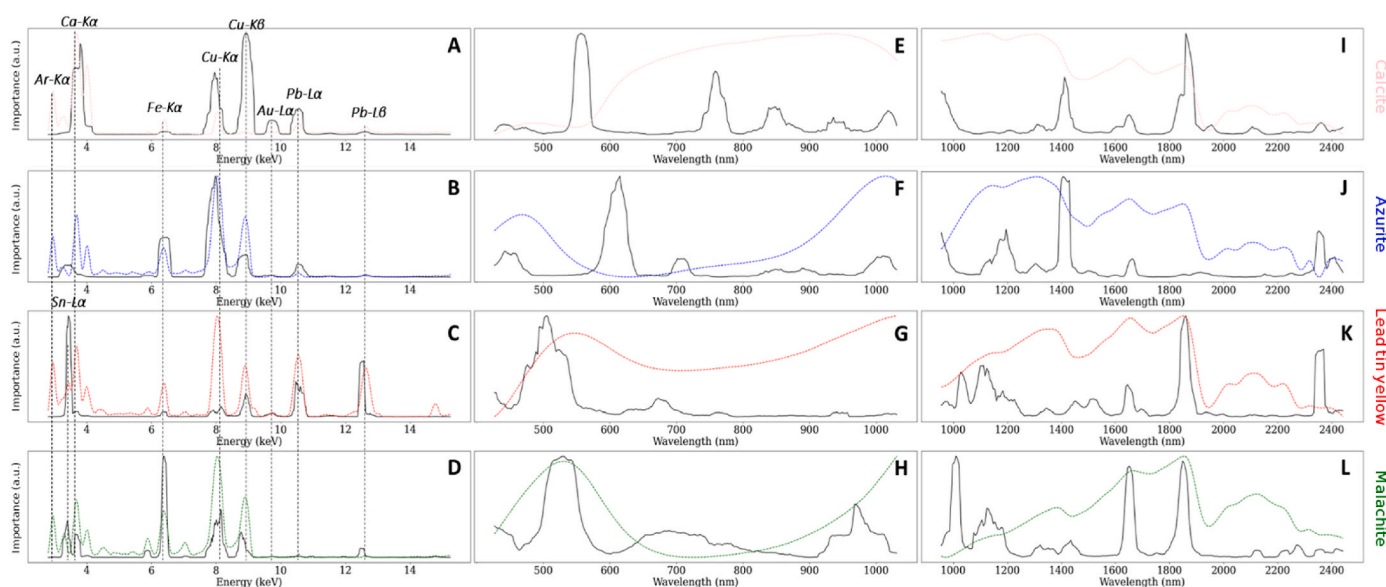


Fig. 4. Feature permutation importance of the log MA-XRF dataset (A–D), VNIR dataset (E–H), and long SWIR dataset (I–L) for calcite (A, E, I), azurite (B, F, J), lead tin yellow (LTY) (C, G, K), and malachite (D, H, L). In color, the average spectrum for the mineral phase is depicted, while the feature permutation importance is shown in black.

(situated around 1201, broad 1500, 1730, 1940, 2040 and 2178 nm). As both SWIR datasets exhibit similar trends, only the long SWIR dataset will be discussed in detail below. The FPI analysis of the models for calcite and gypsum (Fig. 4I and SI-7) are similar to each other. Since the triple degenerate overtones at 1445, 1490, and 1535 nm were not seen in the averaged SWIR spectra of gypsum, also the FPI analysis does not indicate these as important features in the model. The first couple of bands are important for an accurate prediction of calcite and gypsum in the SWIR models. It is interesting to note that the model uses the steep decrease in reflectance located near 1900 nm and not the band related to the support at 1940 nm. The SWIR FPI analysis of azurite (Fig. 4J) identifies important features around 1410–1460 nm, indicating that the steep decrease in reflectance is used by the model, as well as a local

minimum near 1200 nm that can be related to the support. The characteristic wavelength at 1495 nm (i.e., the second overtone of the hydroxyl group) is not fully utilized, as only a very small importance peak is visible. This could be due to the presence of a broad band related to the support in this wavelength region. However, wavelengths associated with carbonate stretching's third overtone around 2350 nm are found as important feature peak. Likewise, the carbonate stretching's third overtone wavelengths are also important for the SWIR prediction of hydrocerussite (SI), another carbonate-containing compound. Other important features for the SWIR hydrocerussite model can be related to the steep decrease in reflectance around 1900 nm and a local maximum (2100 nm) visible in the average spectrum. The two most important features of the SWIR prediction model of lead tin yellow (Fig. 4K) are

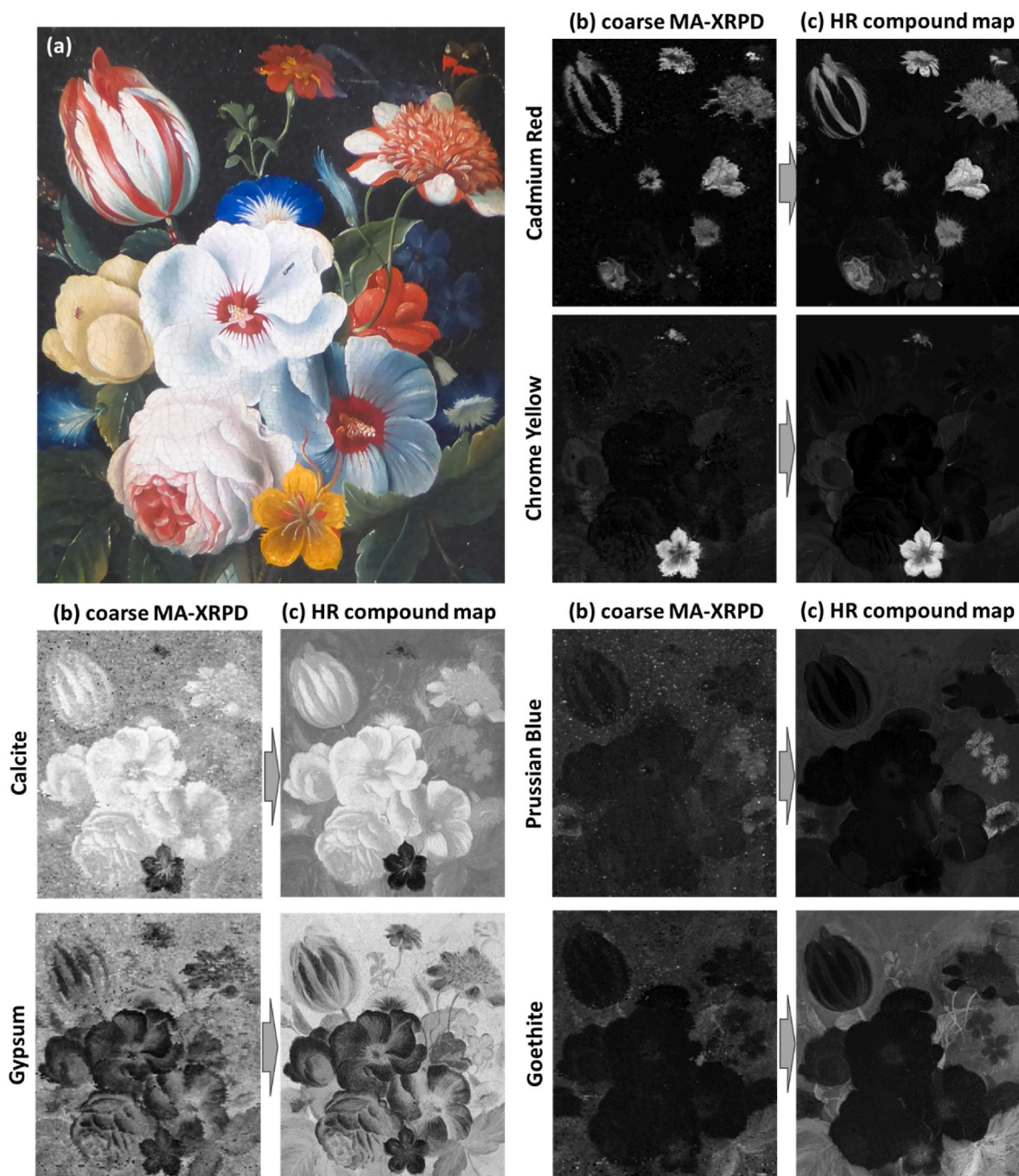


Fig. 5. (a) Central part of the Flower piece painting. Grey scale images of the (b) experimentally recorded ('coarse') MA-XRPD and (c) predicted higher resolution ('HR') compound distribution maps based on the corresponding fitted MA-XRF data.

located at the maximum of the reflectance around 1880 nm and around the carbonate stretching third overtone at 2350 nm. While lead tin yellow does not contain any carbonates, within this dataset it is found colocalized together with the carbonate-containing pigments hydrocerussite and malachite. The SWIR model of malachite (Fig. 4L) shows important features around 1000–1200 nm and 1630–1680 nm. The latter is related to the maximum at 1630 nm. The absolute maximum in average reflectance is also indicated as an important feature. It is interesting to note that the carbonate overtone at 2350 nm is a relatively unimportant feature for the malachite model, while for the other carbonate-containing compounds it was identified as a relatively important band.

3.5. High resolution compound distribution maps from an oil painting

In Fig. 5, a practical use of employing the predictive potential of the above-discussed data-fusion algorithm is illustrated using the flower centerpiece data; six pigment abundance distribution maps are shown. First, the chrome yellow and cadmium red distributions and their predictions are shown as these pigments can clearly be linked to their corresponding elemental (MA-XRF) maps, respectively Pb, Cr and Cd and Se (Fig. SI-1B). Hence, it was assumed that the algorithm would be able to predict their distribution in a straightforward manner. The resulting high resolution compound distribution maps of Fig. 5c indeed exhibit significantly higher spatial resolution and improved interpretability compared to the original coarse, “as collected” MA-XRPD maps of Fig. 5b. The denoising effect that accompanies the resolution enhancement is also clearly evident in this figure. Next, the distributions of calcite, gypsum, Prussian blue, and goethite were considered. Distinguishing these pigments solely based on MA-XRF data is challenging due to their similar elemental compositions: Prussian blue and goethite both show only an Fe–K XRF signal, while for both calcite and gypsum a strong Ca–K signal is obtained, plus a weak S–K signal in the case of gypsum (Fig. SI-1B). Clearly the algorithm is able to predict the distributions with enhanced resolution: both Ca-compounds have complementary distributions, calcite being present mainly in the lighter parts of the flowers and gypsum likely present in the ground layer since its XRD signals are strongest in the darker tones and in the background areas of the painting. While the Prussian blue is mainly present in the blue *forget-me-nots*, the yellow goethite is part of the paint used to render the dark green leaves and is also present in the background. The maps in Fig. 5c clearly demonstrate that by combining high-resolution XRF distributions, in which compounds with a similar elemental signal cannot be distinguished, with low-resolution, compound-specific distribution maps from MA-XRPD, it is possible to create high-resolution, compound-specific and less noisy distribution maps. The high-resolution compound maps allow the details of the pictorial representations created by the artist to be “read” in a much more straightforward manner by heritage professionals such as art conservators and art historians.

It is noteworthy to mention that the MA-XRF scan of the painting, with a resolution three times higher than MA-XRPD, requires about 4.5 h. In contrast, performing the MA-XRPD scan at the same resolution as the MA-XRF scan would extend the acquisition time from 82 h to over 700 h.

4. Conclusion

While macroscopic X-ray powder diffraction (MA-XRPD) has proven itself to be a useful tool for investigating painted works of art, the time required for analyses remains relatively long, typically preventing the analysis of the entire work of art. To overcome this limitation, we employed random forest regression models to predict the abundance of the pigmented compounds within an illuminated manuscript, based on MA-XRF, VNIR (400–1000 nm), short SWIR (short wave infrared: 900–1700 nm), and long SWIR (900–2500 nm) hyperspectral data cubes and within an oil painting, based on MA-XRF data.

From this study, the prediction of quantitative compound distribution maps appears promising. In case the MA-XRPD data is fused to MA-XRF data, reducing the dynamic range of the MA-XRF spectral data improves the accuracy of the models. Depending on the compound, using fitted MA-XRF maps will allow for a more accurate prediction than when the entire (i.e., unfitted) MA-XRF set of spectra is used. When a RIS dataset is used to fuse with MA-XRPD maps, transforming them to their first derivative will affect the prediction performance in different ways. In the VNIR range, employing the first derivative data generally improves the prediction performance, while in the SWIR range the opposite is true. Using a SNV transformation on the RIS data sets generally lowers the accuracy of prediction. Models based on the long SWIR RIS dataset yield more reliable results than those using short spectral range SWIR datasets. It is important to perform a statistical validation, such as the RMSE, in addition to a visual validation. In such manner it becomes apparent where the models fail. In this study the MA-XRF dataset resulted in the best RMSE scores overall; however, when visually comparing the predictions, it is clear that the RIS datasets are better suited for predicting the Cu-containing pigment distributions such as azurite and malachite. Analyzing the FPI of each model revealed that the MA-XRF model uses elemental fluorescence lines for predicting the relative abundance of the different compounds, e.g., for the azurite distribution the most important features are the Cu–K lines. Looking into the FPI of the VNIR datasets spectral features related to the compounds can be used for predicting the relative abundances. In the SWIR range often the most important features for predicting the maps of the different compounds were related to the bands of the support material, which are dominant in most SWIR spectra. Also, when employed for the fusion of data from a 20th century oil painting with relatively simple build-up, the algorithm yielded promising results. A more extensive evaluation of the performance of the algorithm on more MA-XRPD data obtained from more complex 15–17th century paintings is underway and is planned to be published as a sequel (Part 2: case studies) to this paper.

This study introduces novel avenues for research in illuminated manuscripts and oil paintings. Firstly, combining datasets can create new models leveraging the strengths of each modality. Secondly, when more datasets of different illuminated manuscripts are added to train the models, external prediction of compounds in unknown manuscripts becomes feasible, enabling rapid and reliable predictions based on fast hyperspectral methods like RIS or MA-XRF. Thirdly, a more time-efficient investigation of artworks is possible by initially scanning a small portion or performing a coarse scan of the object with MA-XRPD to generate a training set, then predicting compound distributions across the entire object using MA-XRF or RIS data, i.e., internal prediction. Additional research, employing advanced ML techniques like deep learning or spatial data analysis, could further enhance prediction quality.

In a more general way, the authors of this paper extrapolate from the above considerations that machine learning is likely to have a profound impact on the manner in which non-destructive chemical imaging of artworks is going to evolve in the coming decade. Previously, mostly single modality imaging (both RIS and MA-XRF) methods have been used to extract useful information from works of art, there are obvious advantages associated with employing a multi-modal approach: the range of compounds on which distribution information can be obtained is increased while the reliability with which the presence of specific compounds can be detected is augmented. This will motivate researchers and heritage professionals to start using combinations of multiple imaging methods on a more routine basis, either simultaneously or in a sequential manner. Several instruments offering the possibility to simultaneously collect e.g. RIS and XRF or XRF and XRD data have already been described [8,48]. The significant added value of machine learning methods in this context is that they will offer the possibility to transform (in a quasi- or completely automated manner) the ‘as collected’ hyperspectral data blocks into a set of high quality compound maps that are readily interpretable by heritage professionals. On the

other hand, the consistency with which such a transformation can be realized will depend very much on quality, accuracy and scope of the data that is initially employed to train the ML algorithms.

CRedit authorship contribution statement

Arthur Gestels: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Francesca Gabrieli:** Writing – review & editing, Formal analysis, Conceptualization. **Thomas De Kerf:** Writing – review & editing, Formal analysis. **Frederik Vanmeert:** Writing – review & editing, Formal analysis. **Hernan Fernández García:** Formal analysis. **John Delaney:** Writing – review & editing. **Koen Janssens:** Writing – review & editing, Supervision, Funding acquisition. **Gunther Steenackers:** Writing – review & editing, Funding acquisition. **Steve Vanlanduit:** Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Arthur Gestels reports equipment, drugs, or supplies and writing assistance were provided by Netherlands National Museum. Arthur Gestels reports writing assistance was provided by Scientific Research Department at the National Gallery of Art, Washington, DC. Arthur Gestels reports financial support was provided by Research Foundation Flanders. Arthur Gestels reports financial support was provided by Interreg Flanders-Netherlands. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2024.126731>.

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