Journal of Archaeological Science: Reports 73 (2026) 105786

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Characterisation of pigments and technical features of Byzantine mural paintings from eastern Crete (Lassithi): a diachronic view of reds between the 8th and 16th centuries☆

Yiğit Zafer Helvacı [a,1,*], Roberto Giustetto [a,2], Giacomo Chiari [b,3], Tiziana Cavaleri [c,5], Maurizio Aceto [d,4], Klio Zervaki [e], Monica Gulmini [f,6]

[a] Department of Earth Sciences, University of Turin. Via Valperga Caluso 35, 10125 Torino, Italy
[b] The Getty Conservation Institute – GCI (retired), 1200 Getty Center Drive, Suite 700, Los Angeles, CA, USA
[c] Centro Conservazione e Restauro, La Venaria Reale, Via XX Settembre 18, 10078, Venaria Reale, Italy
[d] Dipartimento Per Lo Sviluppo Sostenibile e La Transizione Ecologica (DiSSTE) - Università Degli Studi del Piemonte Orientale "Amedeo Avogadro" Piazza Sant'Eusebio 5, 13100 Vercelli, Italy
[e] Ephorate of Lassithi Antiquities, Archaeological Museum of Agios Nikolaos, Kon. Pal. 74, 72100 Agios Nikolaos, Greece
[f] Department of Chemistry, University of Turin. Via Giuria 7, 10125 Torino, Italy

A B S T R A C T

Crete, the largest and most populous Greek island, occupies a central role in Byzantine art. However, eastern Crete (Lassithi) remains underrepresented in art historical and archaeometric literature, limiting a comprehensive understanding of regional Byzantine artistic practices and their development. To address this gap, this paper documents a systematic, multi-analytical study of Byzantine mural paintings from eleven churches in Lassithi (8^{th} – 16^{th} century). It focuses on the identification and use of red pigments, and aims to characterize the composition and execution techniques of paintings through a combination of in-situ and laboratory analyses consisting of pXRF, FORS, PLM, SEM-EDS, and µXRD.

The results indicate a consistent but variable use of red ochres, vermilion, and red lead. Of these, ochres are the most frequent pigment, appearing in a range of typologies and purity levels. Vermilion, though costly, was more widely used than previously assumed, appearing not only in focal iconographic elements, but also in borders and underlayers. Red lead was also found in mixtures and degraded layers. Data relating to the lime-based matrices suggest the common use of *a secco* technique, with painters adapting their approach based on material and visual requirements.

The results show local continuity in pigment choices and application, with gradual changes over time, contributing new insights into the technical features of Byzantine mural paintings of the region, along with a valuable reference dataset. In addition, several degradation phenomena identified in this study, including the thermally induced pigment transformation and humidity-related chromatic alterations, carry direct implications for conservation practice.

1. Introduction

1.1. Context and Byzantine art in Crete

The religious aspect in Byzantine art is widely acknowledged as central, and icons and sacred images remain at its core, representing media through which the divine presence could be conveyed and mediated (Gombrich 1951; Cormack 2000). Art historical discourses generally tend to prioritize hagiographic and iconographic surveys and discussions at the expense of material inquiry. At the same time, the historical and cultural significance of these paintings is equally embedded in their physical execution processes. The materials and techniques used in the creation of liturgical visual media should also be considered relevant sources of information for a thorough

☆ This article is part of a special issue entitled: '8th ARCH_RNT Proceedings - Archaeomaterials' published in Journal of Archaeological Science: Reports.

* Corresponding author.
E-mail address: yigitzafer.helvaci@unito.it (Y.Z. Helvacı).
[1] 0000-0002-7946-3010.
[2] 0000-0003-4131-2169.
[3] 0000-0003-4707-3816.
[4] 0000-0002-5206-6170.
[5] 0000-0001-6360-3632.
[6] 0000-0002-0556-5401.

https://doi.org/10.1016/j.jasrep.2026.105786
Received 7 August 2025; Received in revised form 3 April 2026; Accepted 21 April 2026

understanding of the overall significance of the paintings within their historical and cultural contexts.

Byzantine paintings have been the subject of extensive scientific investigations, yielding significant insights into the material characteristics and production techniques. In literature concerning the archaeometric study of Byzantine art, greater attention appears to have been given to portable icons, although a significant number of mural paintings have also been analysed (Daniilia et al. 2008; Sophia Sotiropoulou and Daniilia 2010; Kakoulli et al. 2012; Mastrotheodoros 2018; Nicola et al. 2018; Mafredas et al. 2021). At the same time, the region of eastern Crete (Lassithi prefecture; Λασίθι) has remained substantially underrepresented from both materials and art historical perspectives, despite its considerable significance. According to early surveys for Crete, over 800 churches dating to the period between 1225 and 1523 were listed (Gerola 1917). Later inventories and lists of churches in Crete expanded this list, and Bissinger (Bissinger 1995) further increased this number to nearly a thousand churches with mural paintings, remarking that such a number amounts to almost half the total number of churches found throughout Greece (Kalokyris 1957; Spatharakis 2001). However, these surveys focused mainly on the central and western parts of Crete. At the same time, the small number of Lassithi churches in the inventories falls short in representing the actual volume and richness of the region's Byzantine heritage.

The churches in eastern Crete are characteristically small and regional in scale, remaining humble and provincial over time (Kalokyris 1957; Lymberopoulou 2016a, 2016b). Most are single-aisle buildings, built from local materials with some imported carved stone elements (door jambs, lintels, window frames). Masonry is composite, combining brick, stone, and marble. Their most significant feature for this study is their interior decoration: mural paintings that often cover entire inner wall surfaces.

Up until the 8th century, evidence of Byzantine activity in Crete is limited to church plans and related surviving floor mosaic decorations, with little physical remains in terms of mural paintings. To these architectural plans in the Lassithi context, the early Christian basilica remains in Elounta, Pseira Island and Itanos can be pointed out. Generally, the remains in the Church of St. Anne in Nefs, Amari (central-western Crete, near Rethymno), dating to 1225, are considered as the earliest mural paintings (Spatharakis 2001). Over the following centuries, the painting style evolved stylistically, absorbing influences from Constantinople and reflecting successive Byzantine artistic movements, such as Macedonian, Komnenian, and Palaiologan. Most surviving paintings date to the Venetian period (Venetokratia), often termed Late Byzantine or early post-Byzantine, and blend traditional Byzantine iconography with Constantinopolitan and Western influences. The 15th century marked the emergence of the Cretan School of icon painting, which became a driving force in Orthodox art and positioned Cretan Byzantine painting as part of the broader European Renaissance artistic landscape.

The historical and social reasons behind such an abundant and intense artistic activity across Crete are the island's centrality in the Mediterranean and the political and cultural interactions taking place there, especially after the island's capture by the Venetians in the 13th century and the subsequent emergence of the Cretan school of icon painting from the 15th century onwards. Documentary evidence indicates the presence of Cretan painters in Venetian archives, attesting to a developed and organized patronage and artistic culture (Marković 2016). In this context, academia has also addressed the historical and economic aspects of Cretan church building and painting activities (Lymberopoulou 2016a, 2023), as well as the analyses of the materials in portable icons attributed to the Cretan school and its prominent artists, such as Angelos Akotantos (Mastrotheodoros et al. 2020). Studies focusing on the historical context, materials and techniques of Byzantine mural paintings in churches in Crete include the analysis of mural paintings from Patsos and Meronas (Rethymno region, western Crete) and the Byzantine Mitropolis basilica at Gortyna (southern Crete) (Westlake et al. 2012; Cheilakou et al. 2014), as well as a recent extensive historical and field survey (Despotakis and Tsamakda 2023). In particular, however, case studies from Lassithi are not dealt with in the current archaeometric literature, to the best of the authors' knowledge.

1.2. Aims of the study

To address the above-mentioned gap in literature, this study presents a multi-analytical investigation of Byzantine mural paintings from eleven churches located in Eastern Crete, dating to the period between the 8th and 16th centuries CE. It is part of a broader interdisciplinary project aimed at a thorough architectural survey of selected churches in Crete using AutoCAD, their photogrammetric reconstruction, photographic documentation, technical photography survey, and scientific analyses, both in situ and in the laboratory, of the materials and techniques used in mural paintings. Due to the large amount of collected data and resulting information, this paper has been focused only on the red hues, which exhibit significant chromatic variation resulting from the use of diverse materials and specific technical choices. These complexities warrant a dedicated and in-depth investigation, with the aim of characterizing the materials and execution techniques, while tracing both changes and continuities in the choice of pigments, their morphological and chemical characteristics, and application across time. To this end, a combination of *in-situ* and laboratory analyses was employed, including portable X-Ray fluorescence spectroscopy (pXRF), polarized light microscopy (PLM), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray Diffraction, and fiber optic reflectance spectroscopy (FORS), enabling comprehensive characterization of the red pigments and their application, and yielding valuable insights into the material technical characteristics of the Byzantine mural paintings of the region.

The project's systematic approach extended the survey across a period of nearly eight centuries, allowing a bottom-up approach in ascertaining the material and technical characteristics of the related hieratic painting traditions in Lassithi. Similar efforts were previously made on Byzantine mural paintings from Cappadocia, allowing a complete understanding of the materials used in murals from a specific region (Pelosi et al., 2013). Similarly, Westlake and colleagues analysed fragments of mural painting from Crete dating to different periods – such as Minoan, Roman, Late Antique, and Byzantine- to define a continuity for raw material choices and techniques (Westlake et al. 2012).

On the macro-level, the outcomes of the analyses might be used to support future conservation interventions and to plan correct and efficient methods for the safekeeping of the mural paintings. On the micro-level, the diachronic aspect evokes questions of change and continuity, in terms of raw material choices and modus operandi of the artists across the centuries. We consider a set of paintings fully grounded in the Byzantine tradition, with minor elements suggesting a kind of resistance or, in other terms, inertia to potential cultural and artistic influences from the West.

The search for a commonality or tradition in terms of what constitutes the material and technical characteristics of Byzantine mural paintings is a topic frequently touched on by the current literature, and considerable efforts have been made to address the emerging research questions (Dionysius of Fourna, 1989; Winfield 1968; Mora et al. 1984; Mafredas et al. 2021). In this context, one of the main goals of this study is the provision of representative material and technical data from a specific geographical region across time, that can be considered through the lens of tradition, continuity and change. Given the scarcity of substantial textual evidence concerning the technical part of Byzantine paintings, archaeometric investigations are pivotal to support the understanding of the material and technical characteristics of these murals beyond the naked eye. The acquisition of such datasets, therefore, proves to be an indispensable tool in discerning characteristics that can be attributed to certain traditions, locations, or periods.

2. Materials and methods

2.1. Churches and mural paintings examined

The mural paintings investigated in this study are located in small to mid-scale churches in the eastern region of Crete, within the boundaries of the Lassithi prefecture (Fig. 1). The earliest church dates back to the 8th century, and the most recent to the late 16th century (Table 1). For selecting mural paintings to be analysed, the following criteria were adopted: i) chronological coverage (to represent all possible periods); ii) features and iconographic diversity (to capture the widest range of artistic styles); iii) geographical coverage across the region (to ensure representativeness). No selection criteria were applied in churches with only one panel; in other instances – e.g., at Panagia Kera, four different panels were chosen to reflect its stylistically and chronologically distinct paintings. In fully decorated interiors, the largest feasible area was surveyed. Practical constraints such as site accessibility, time availability and the logistics of fieldwork in remote locations, also affected the final selection.

Similar to the characteristics observed in other regions of Crete, the architectural size and scale of the churches included in this study are modest in scale. One significant feature is the double-church and two-aisled church plans that are characterised by bipartite liturgical spaces, often constructed to serve both the local Orthodox and Venetian communities under the same architectural structure (Gediminskaite 2019; Lymberopoulou 2016b). For instance, the Church of St. George and St. John Theologos in Voila (Handras, Sitia) features a double-church plan, with two separate bemas, apses and roofs for each section, dedicated to a different saint (Patedakis 2015). On the other hand, the northern side aisle of the Church of St. Paraskevi in Ziros, hewn into the natural bedrock, presents an in-between form between the two-aisled church plan and other traditional monoapsidal structures. An exception to the simple church plans is represented by the 12th century Church of Panagia Kera, in Kritsa, originally a single-aisle church that was transformed into a larger three-aisled domed basilica through modifications completed in the 14th century (Mylopotamitaki 2005).

The iconography of the mural paintings predominantly features

Table 1
List of churches from eastern Crete region (Lassithi), included in this study.

Church name	Location	Chronology	Area	Coordinates
Church of St. Nicholas in Ormos	Ag. Nikolaos	8th – 14th c.	Agios Nikolaos	35°12′14.10″N; 25°43′3.46″E
Church of St. Stephen	Monastiraki	11 – 13th c.	Hierapetra	35° 4′50.36″N; 25°49′33.86″E
Church of Panagia Kera	Kritsa	13 – 14th c.	Agios Nikolaos	35° 9′24.37″N; 25°39′18.60″E
Church of Panagia Faneromeni	Skopi	14th c.	Sitia	35°13′9.51″N; 26° 3′43.26″E
Church of St. Nicholas	Ziros	14th c.	Sitia	35°4′30.31″N; 26°8′27.29″E
Church of St. George	Skinokapsalo	14 – 15th c.	Hierapetra	35° 3′13.34″N; 25°53′11.45″E
Church of Panagia Eleousa	Papagiannades	14 – 15th c.	Sitia	35° 5′46.68″N; 26° 4′12.19″E
Church of St. George in Exo	Mouliana	15th c.	Sitia	35° 9′55.67″N; 25°59′16.69″E
Church of St. George and St. John T/logos	Voila	16th c.	Sitia	35°5′7.55″N; 26°6′23.41″E
Church of St. George	Epano Simi	15th c.	Hierapetra	35° 2′47.62″N; 25°29′50.12″E
Church of St. Paraskevi	Ziros	16th c.	Sitia	35°4′30.36″N; 26°8′24.16″E

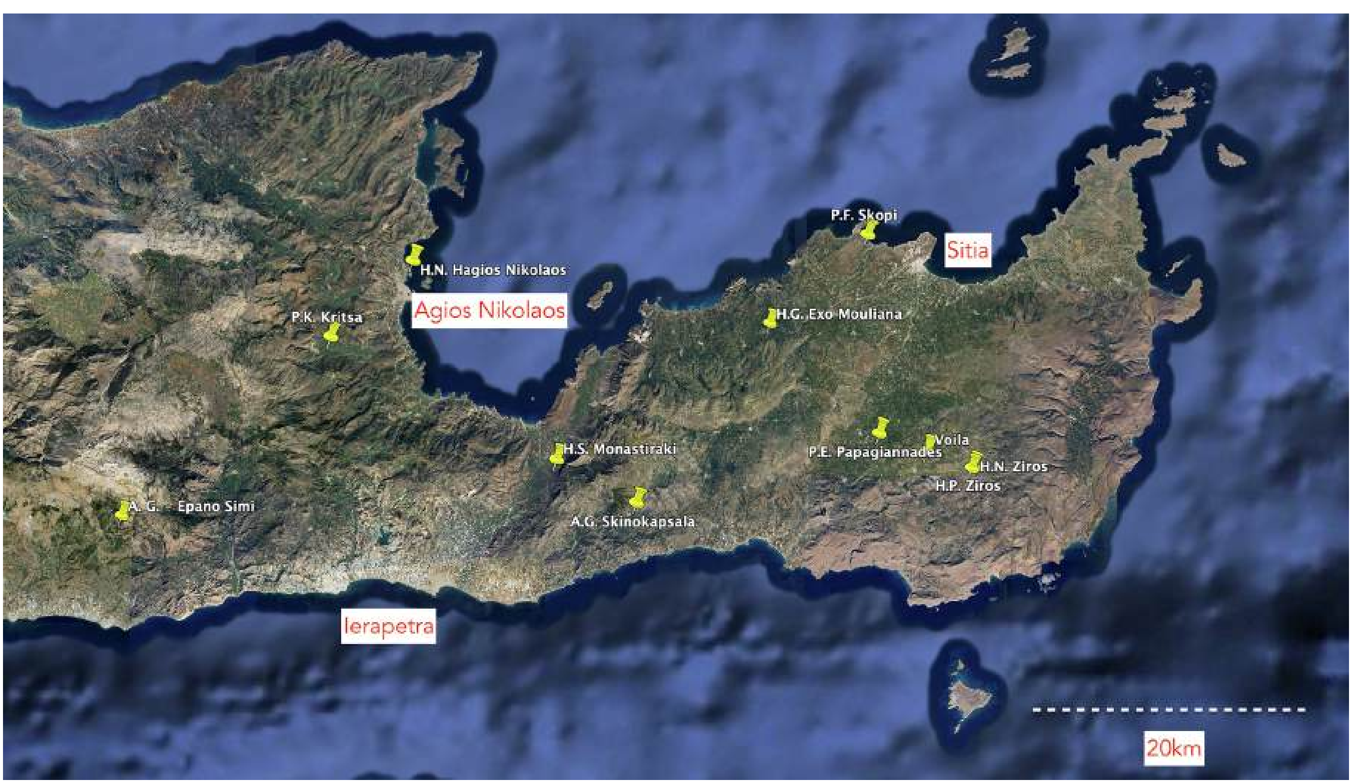

Fig. 1. Map of eastern Crete (Lassithi Prefecture) indicating the present-day towns of Agios Nikolaos, Hierapetra and Sitia; and locations of churches included in this study. Map .
Source: Google Earth Pro 2025

Byzantine characteristics and adheres to Orthodox traditions, albeit with some variations and exceptions. The oldest mural paintings considered in this study (8th century) exhibit a distinct geometric style, primarily associated with the Iconoclastic Period (Church of St. Nicholas in Ag. Nikolaos). Another exception, the 16th century mural panel from the church dedicated to St. George and St. John Theologos depicts the Virgin Mary and the Infant Jesus in the “Seat of Wisdom” (*Sedes Sapientiae*), which is less closely linked to Byzantine tradition and more to Western contexts, such as the mosaic panel in the Basilica of Sant'Apollinare Nuovo in Ravenna (6th century), or the wall painting from the lower church of St. Clementine in Rome (8th century). Other subtle Western elements and references are present throughout the painting programs. A relevant example is the depiction of Western clergy in scenes of Hell, Venetian-glass tableware or of St. Francis (Church of Panagia Kera in Kritsa), a figure generally associated with Western tradition (Klontza 2008).

2.2. Analytical techniques

The study of the mural paintings was carried out using a multi-analytical procedure, preceded by a thorough examination of the painted surfaces with the naked eye and photographic documentation under both visible and UV light. Images in visible light were acquired by positioning the light source in both direct and raking angle configurations to capture as much morphological detail as possible from the surface, using both a 16-megapixel and a 48-megapixel digital camera mounted on a tripod. UV-induced fluorescence images were taken with the 16-megapixel camera, illuminating the paintings with a portable 10-watt TATTU 365 nm UV light source fitted with a ZWB2 filter. This first step guided the selection of specific points of interest, which were further documented with a Dino Lite AM4113T digital portable microscope (DPOM) equipped with a 1.3-megapixel sensor and up to 200x magnification.

This preliminary inspection provided information that supported the identification of painting/repainting sequences, if present, and highlighted topographical features of the surfaces related to the manufacturing process, such as incisions, compass lines, *pontata* or *giornata* joints, as well as any visible preparatory drawings (*proplasmos*). Microphotographs taken under the digital microscope highlighted overlaps in the chromatic layers and some morphological characteristics of the pigment particles dispersed in the paint matrix.

A Bruker Tracer III SD portable X-ray fluorescence spectrometer (pXRF), equipped with a silicon drift detector (SDD) and mounted on a tripod, was then used to determine the elemental composition of selected spots, to gather elemental information at the bulk level, which can be indicative of the pigments. The following standardized parameters were used for the acquisition: 40 kV; 12 μA; filter/collimator: (no); and 120 s of acquisition time. The pXRF raw data was then processed using the Bruker Artax 8 software.

The pXRF spectra were post-processed for visualizing the spatial distribution of pigments across the mural paintings. To this aim, elemental distribution maps were generated using SmART_scan software (Martin-Ramos and Chiari 2019). The program interpolates elemental or molecular composition data acquired at discrete points (e.g., by XRF, XRD, Raman) across the complete surface of the digital image of the mural painting surface (visible, infrared, ultraviolet, X-ray radiography, etc.) as spatial references. The software extrapolates and calculates false-color composition (FCC) maps by minimizing the Euclidean distance in a multidimensional color space (up to 15 dimensions), resulting in a detailed mapping of pigment spatial distribution. Boolean operators (<AND>, <OR>, <NOT >) allow for mapping co-occurrence or exclusion of elements/compounds, and the software supports integration of multiple analytical techniques.

The outcomes of the preliminary non-invasive approach guided the preparation of a targeted sampling campaign aimed at collecting representative micro-samples (μ-sample – μ-fragment) to be analysed in the laboratory (Table 2). By doing this, the main criterion was the collection of samples from damaged areas and *lacunae,* although the removal of μ-fragments from degraded areas might have compromised the sample integrity and intonaco extraction (Sandu et al. 2012; Tsang et al. 2019; Caple and Williams 2000). The second criterion was the actual color of the area, optimizing the amount of information by selecting points where multiple layers could be observed (Fig. 2). Representative μ-fragments (1—1.5 mm in size) were removed using a scalpel, detaching the complete sequence of the painting layers and, whenever possible, also including a small portion of the support (*intonaco*, whitewash), in order to gain meaningful data about the whole stratigraphy (Caple and Williams 2000). Following the extraction, the samples were placed in Eppendorf tubes.

The samples were initially inspected under a Leica Stereozoom microscope to highlight their morphology and features, including the number and orientation of the layers. UV–Vis-NIR reflectance spectra were then recorded from both sides of the detached samples using Fibre Optics Reflectance Spectrometry (FORS) for preliminary characterization of the colourants. FORS analyses were performed by an Avantes (Apeldoorn, The Netherlands) system combining an AvaSpec-ULS2048XL-USB2 spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source, connected by an FCR-7UV200-2–1.5x100 fiber optic probe. The system was controlled by AvaSoft v.8 software, running on Windows. The overall operational range was 375–1100 nm, with 2.4 nm as the best spectral resolution, calculated as FWHM according to the monochromator (slit width 50 μm, UA-type grating with 300 lines/mm) and the detector (2048 pixels) characteristics. Diffuse reflectance spectra, referenced against the WS-2 reference tile provided by Avantes (≥98% reflectivity), were recorded by positioning the probe at a 45-degree angle to the surface. Total acquisition time was 1 s per spectrum, resulting from 100 scans with 10 ms integration time. For the detection of mineral phases present, Micro(μ)-X-ray diffraction (XRD) data were collected by analysing the untreated μ-fragments with a SMARTLAB XE-Rigaku diffractometer in μ-diffraction mode and zero background, Si monocrystal flat sample holder, in the 3 to 70° 2-Theta range using monochromatized Cu Kα radiation.

The samples were then prepared as cross-sections by embedding the fragments with the proper orientation into Struers Epofix resin, and subsequently abrading and polishing them using Struers RotoPol and silicon carbide abrasive sheets, with grit levels ranging from 500 to 4000. The cross-sections were then studied using an Olympus B50X polarized microscope in dark field light configuration, at magnifications between 40x and 500x, with the 200x configuration providing the most informative images. The cross-sections were further examined using a JEOL (Akishima, Japan) JSM-IT300LV scanning electron microscope (SEM) in backscattered electron mode, coupled with an energy dispersive spectrometer (EDS) equipped with an SDD detector (Oxford Instruments, Abingdon, UK), using 20 KeV acceleration voltage at a working distance of 10 mm. The SEM data was processed and interpreted using the Oxford Instruments AZtec software v. 6.1 for the chemical and morphological analysis of the cross sections, as well as for the acquisition of BSE elemental maps and EDS point analysis spectra.

3. Results

3.1. Photographic documentation and in-situ surveys

The preliminary inspection of the paintings revealed a wide range of red colours, ranging from deep crimson to light-red and even pink. In the post-15th-century mural paintings investigated, red frequently emerged as a dominant colour, fulfilling both decorative and symbolic functions. It was encountered in themes such as martyrdom, divine presence, and the sacrifice of Christ (Wreschner et al. 1980; Miller 2000; James 2003; Jeffreys et al. 2008; Popelka-Filcoff and Zipkin 2022). The use of red pigments in a naturalistic manner is also encountered, in depicting objects that are red in reality, such as floral scenes, blood in crucifixion

Table 2
List of micro-samples. In addition to the samples' identifier codes, their physical context, and stratigraphic structure, the "Reference in Text" column provides a cross – reference to the pertaining visual data provided in figures. The "Available Visual Information" column provides a brief description and context of each cross section that is discussed in other sections of the article.

Sample	Church	Location	Stratigraphy	Reference in Text (Figures)	Available Visual Information
HNZ 1	St. Nicholas in Ziros	Nave N wall	Single + intonaco	2, 8	Chunky quartz grains, candle burn
HNZ 8			Multiple + intonaco		*Incarnation, a secco* technique, pigments in Ca matrix
HP 2	St. Paraskevi in Ziros	Main panel E entrance	Multiple + intonaco		3 tone painting style – white highlight
HP 1/0					Amorphous red ochre matrix
V 2	St. Geo. & St. Io. Voila	Main panel S wall	Multi., no intonaco	2, 11	Red superficial layer degradation
V 4				2, 10	Multi grain ochre, amorphous ochre matrix
V 1 g				2, 8	Larger hematite particles = darker hue
V 1x				2, 11	Degradation of red lead
PPG 1/0	P. Eleousa in Papagia.	Nave S wall	Multi., + intonaco	2, 8	Hematite particles
SK 3	St. George in Skinokap.	Nave N wall	Multi., no intonaco		Use of hematite particles in admixtures
HNN 1	St. Nicholas in Ormos (Ag. Nikolaos)	Main panel N wall	Single + intonaco	2, 8	Amorphous ochre matrix / chunky quartz particles
HNN 7				2, 10	Multi grain ochre, amorphous ochre, hematite particle
HNN 7A					Multi grain ochre, amorphous ochre, hematite particle
MON 1	St. Stephen in Monast.	Apse	Multi., + intonaco	2, 10	Multi grain ochre,
EM 2—1	St. George in Exo Mou.	Main panel S wall	Multi., + intonaco	2, 11	Vermilion in various stratigraphic configurations
EM 6			Single., + intonaco	2, 8	Multi grain ochre, amorphous ochre matrix
EM 1–1			Multi., + intonaco	2, 11	Vermilion in various stratigraphic configurations
PKP3 – 3	Panagia Kera Panel 3	Central Nave S wall	Multi., + intonaco	2, 8	Multi grain ochre, amorphous ochre matrix
PKP4 – 5	Panagia Kera Panel 4	S Transept corridor	Multi., no intonaco	2, 11	Vermilion in various stratigraphic configurations
PKP4 –7a			Single., + intonaco	2, 13	Red ochre thermal degradation, multi-phase
PKP4-7b			Single., no intonaco		
EPS 2	St. George in Epano S.	Nave N wall	Multi., + intonaco	2, 11	Vermilion sublayer for incarnation
EPS 2/o				2, 10	Multi-grain ochre particle

scenes, and fire in the representations of hell (Figs. 2 and 3).

The preliminary survey and documentation of the mural paintings revealed a high level of diversity and creativity in the use of red in mural paintings across centuries. From the outset, single-tone red borders (often flanked by two thin white strips) are an essential and symbolic feature of the paintings' visual language, as they mark, separate, and limit the physical space of the visual narratives, even in single panels (Fig. 3 Box A). Single-tone reds also appear in drapery and cloaks, floral motifs (Box C), and vast background areas, such as hell scenes (Box E). For example, in the churches of St. George in Epano Simi in Hierapetra, and Panagia Kera in Kritsa, the hell scenes are depicted by using bright red backgrounds, with the silhouettes of the people sketched over using darker red brush strokes (Box E). Single tones were also used for finer details, such as fruits on trees (D), stirrups (F), yokes (G), inscriptions, crowns (B, H), and bibles (I).

In at least three of the studied churches, abrasion and flaking of the chromatic layers revealed the use of red pigments directly on the support layer, in the form of light brushstrokes for preparatory drawings (*proplasmos*), thus providing information about the stratigraphic structure of the chromatic layers (Fig. 4) (Weyer et al. 2015; Winfield 1968).

In the investigated paintings, the Byzantine three-tone system is widely used to render shading and modeling of human figures, garments, and draperies (Fig. 5) (Winfield 1968; Oriols et al. 2023). It is an ancient technique, appearing in late antique, medieval and later treatises such as Heraclius De Coloribus, Dionysios of Fourna, Theophilus and later Cennini (Cennini 2014; Dionysius of Fourna 1989). The technique consists in applying an overall ground colour (1st tone), with lighter areas rendered through the addition of white and shadows by adding a darker hue (2nd tone); further highlights are rendered in white or a lighter colour (3rd tone).

3.2. In-situ spectroscopic and laboratory analyses of red pigments

3.2.1. Red ochres

Red ochres could be easily identified through pXRF, which reveals the signals of Iron (Kα1 and Kβ1 peaks at 6.4 keV and 7 keV, respectively), providing a preliminary identification of the pigment group (Bakiler et al. 2016; S. Sotiropoulou et al. 2008; Fioretti et al. 2023). The presence of other related accessory elements, such as Si, Al, and Mn in the pXRF spectra, is normally interpreted as a marker for natural ochres (Bikiaris et al. 2000; Hradil et al. 2003; Eastaugh et al. 2004; Elias et al. 2006). These spectra were systematically recorded in all analysed mural paintings on red areas, suggesting a continuous use of these pigments in the region over time (Fig. 6). The presence of red ochres was also corroborated molecularly by FORS by analysing the individual red strata from μ-samples: spectra showed broad absorption bands in the 535–550

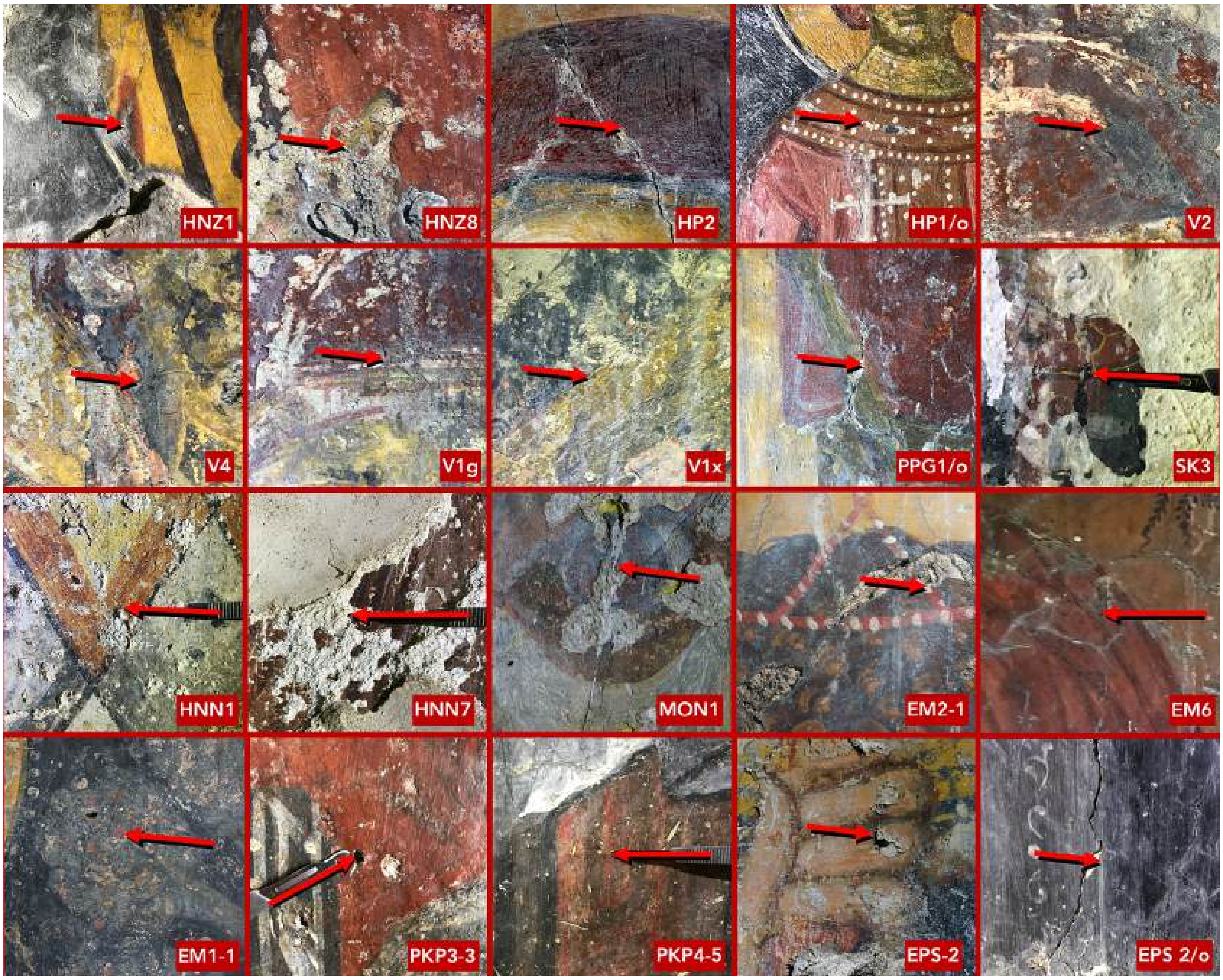

Fig. 2. Close-up (macro) images of the sampling points, illustrating their location within the painted surface (Images: Y. Z. Helvacı). The images also document the variable conservation state of the mural paintings, with some surfaces exhibiting lacunae, salt formations, abrasions, and flaking.

nm range, related to Fe^{3+} electronic transitions (Picollo et al. 2002; Helwig 2007; Aceto et al. 2014). Absorption maxima indicative of Fe-oxides were also visible in the 850–900 nm range, typically associated with red-ochres (Fig. 7).

In terms of chemical composition and morphology, the PLM and SEM data collected on μ-samples predominantly revealed two primary distinguishable forms of ochre-based reds: i) amorphous oxy-hydroxide phases, with fine-grained or larger-sized particles, and ii) anhydrous crystalline Fe-oxide, in the form of hematite (Fe_2O_3). As far as the first form (Fig. 8) is concerned, different hues and intensities of the red colour depend mainly on the grain size of the amorphous Fe-oxy-hydroxides, and secondarily on the addition of other pigments (such as C black) and impurities as well. As a rule, the smaller the grain size, the lighter the resulting red hue was (Helwig 2007). This can be observed in samples for which a larger grain size corresponds to a darker red hue (Fig. 8, Box D, I and J). On the other hand, a finer grain-size of the ochre amorphous particles observed (for example, Fig. 8, Boxes B, H, and F) gives an evident lighter red hue. The same situation is also observed in the related cross sections, in which individual large and discernible dark red hematite crystals are embedded within a finely grained ochre matrix, showing a lighter hue.

EDS-maps of the amorphous red-ochre matrices exhibit a homogeneous diffusion of lower Fe-containing particles across the samples, though sporadic high-Fe bearing particles also appear (Fig. 8, Boxes A, B, D, F, G, H, I and J). As far as Si and Al are concerned, these accessory elements are often coupled to Fe, suggesting they might belong to minor compounds intimately related to red ochres. The amorphous nature (or very low crystallinity) of these materials is testified by a suboptimal XRD response (Mastrotheodoros and Beltsios 2022), whereby the acquired diffractograms are predominantly characterised by calcite and other clay minerals unrelated to the observed red colour.

As far as the second form of ochres (purer and anhydrous crystalline Fe-oxide – in the form of hematite) is concerned (Fig. 8, Boxes A, B, E, and G), Fe_2O_3 crystals are readily identified by PLM and SEM-EDS. The morphology and size of hematite crystals vary highly in the analysed mural paintings, depending on the source, technique, and manufacturing processes. However, some of their typical features, such as tabular habit, trigonal symmetry, and intense red colour, are recognized in all inspected cases.

In the examined cross sections, hematite does not appear to have been used in its pure form as a pigment. Instead, crystals of hematite (varying in size, colour, and purity) were observed, typically embedded within layers of amorphous oxy-hydroxide phases of red ochres, as well as in strata containing other colours such as black, green, and yellow (Fig. 8, Boxes A, B, and G). Elementally, the hematite grains in this study were categorized into two general groups based on their relative Fe content expressed as a mean value, indicating their purity: (a) high Fe content particles with Fe $>$ 75 wt%; (b) moderate Fe content particles with Fe $>$ 50 wt% and $<$ 75 wt% (Fig. 9).

In at least four of the studied churches, ochre grains with characteristic multiple-phase structures were detected, embedded within the support layer or in layers relatively closer to the support layer. Their

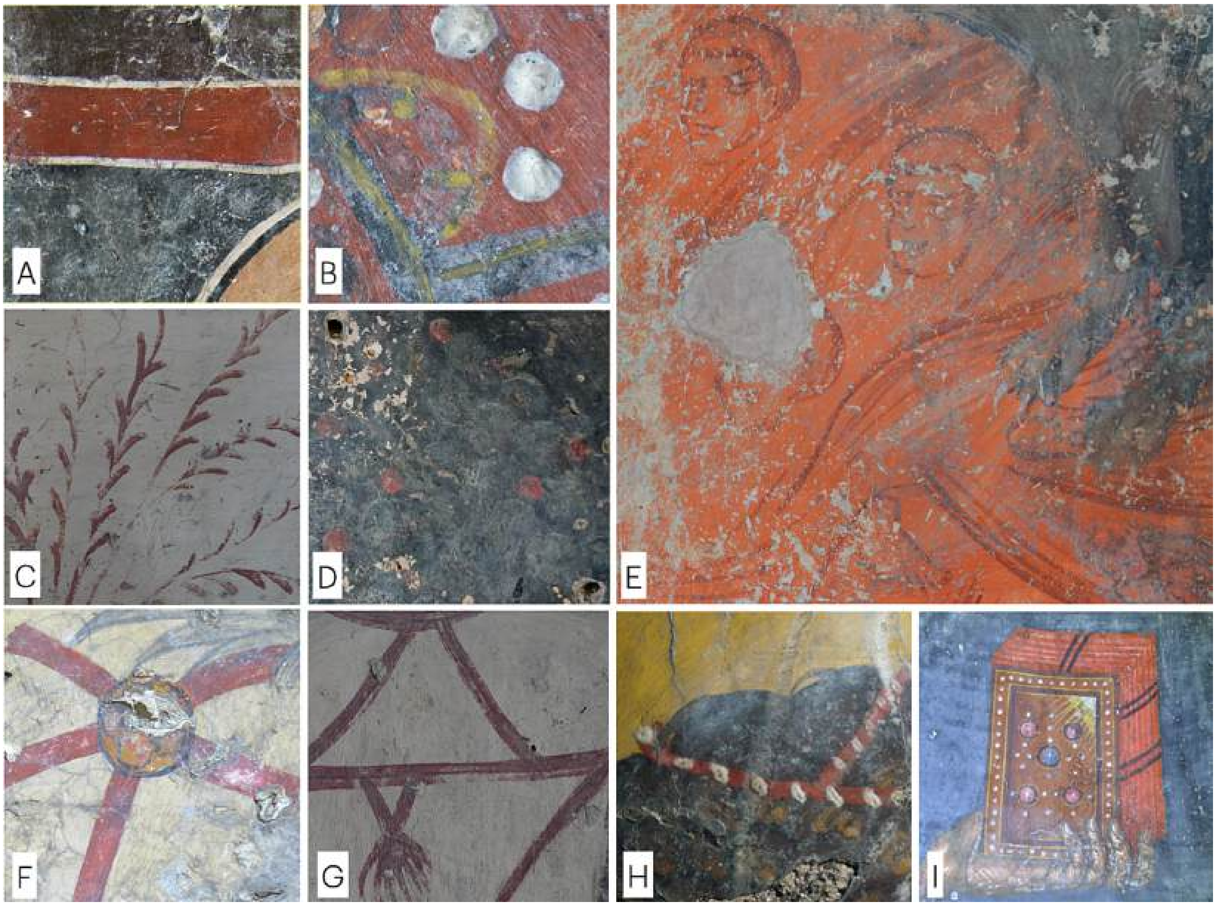

Fig. 3. Photographic documentation of the mural paintings, focusing on the diverse utilisation of red pigments in different contexts. Boxes A and B: Church. of St. Nicholas in Ziros; C: Church of Panagia Kera in Kritsa; D and H: Church of St. George in Exo Mouliana; F and G and I: Church of St. George in Epano Simi. (Images: Y. Z. Helvacı).

Fig. 4. Technical photography (visible light) documentation of the chromatic layers and execution techniques: Top left: Church of St. Nicholas in Ziros, N wall upper vault. Center and right: The Church of St. George and St. John Theologos in Handras, Voila. Due to the abrasion and flaking of the paint layers executed in secco, the preparatory drawings applied with red- ochres, confirmed by pXRF, could be observed (Images: Y. Z. Helvacı).

composite structure, already visible in PLM, becomes evident at SEM, where BSE images show the presence of different minerals (e.g., in the μ-sample from the Church of St. Paraskevi in Ziros) (Fig. 10). The related EDS data show a unique elemental profile, different from that of the superficial red layer, consisting mainly of Ca, Fe, Si, Al, K, and Mg. These multi-phase grains were so far detected in churches dating to the 13th, 15th and 16th centuries.

3.2.2. Vermilion (cinnabar)

Vermilion (cinnabar: mercuric sulphide (HgS)), a pigment widely used since ancient times in the Eastern and Western contexts with desirable characteristics (such as deep red hue, gloss, good covering properties and adhesive strength), is the second most frequently encountered red pigment in the analysed mural paintings and samples (Rutherford et al. 2007; Trinquier 2013; Nöller 2015; Gliozzo 2021). Both names, vermilion and cinnabar, are typically encountered in the literature. Nevertheless, in the mineralogical and crystallographic sense,

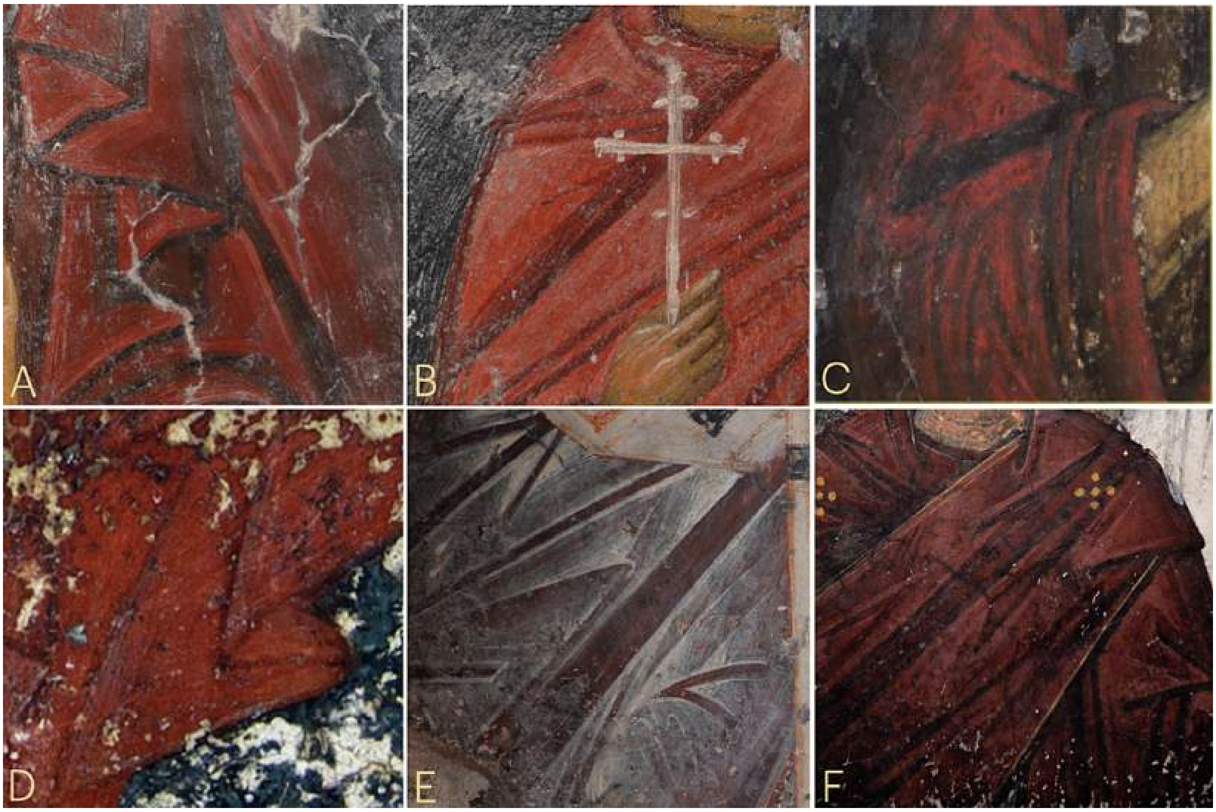

Fig. 5. Photographic documentation, for the application of the three-tone system. In the church of St. Paraskevi in Ziros, this technique was used to a further extent (Fig. 8 Box D for the cross section), where up to five different tones of red, mainly of red ochres, were achieved through layering and mixing of red ochres with other pigments such as C black and Ca white (Boxes A and B). Box C illustrates the use of a recipe with higher vermilion content used in combination with C blacks for achieving the 'shot silk' effect. Box D illustrates the cloak of St. George (Church of St. Nicholas in Ziros), where the mid tone reds were modified through a darker tone for painting the shades. In this context, the pXRF measurements from the mid tone red and darker areas did not reveal any major differences in terms of the elements present, pointing to the use of a C black – enriched paint layer for the darker areas. Box E and F: Church of St. George in Epano Simi, layering system applied with the use of lime white (Images: Y. Z. Helvacı).

the term cinnabar refers to the naturally occurring mineral and, in the arts, to the use of the mineral as a pigment. Since the 1960 s, on the other hand, the name vermilion alludes to the synthetic mercuric sulphide (Rutherford et al. 2007; Nöller 2015; Thompson 2019; Thompson Jr. 2020). Because of the scarcity of natural sources and the fact that the preparation of the synthetic HgS-based pigment (vermilion) was already known and widely used since Roman times, it is more than reasonable to assume that it was the synthetic version mainly used in paintings. Therefore, the term vermilion will be used henceforth to refer to this pigment.

The presence of vermilion was primarily detected *in-situ* by pXRF (Fig. 6) through the detection of Hg ($L\alpha_1$ and $L\beta_1$ peaks for mercury at 9.9 keV and 11.8 keV respectively) and S ($K\alpha_1$ and $K\beta_1$ lines at 2.3 keV and 2.4 keV respectively) (S. Sotiropoulou et al. 2008; Bakiler et al. 2016; Armetta et al. 2021). Additionally, SEM-EDS mapping confirmed the presence and distribution of mercuric sulphide particles, through the Hg $M\alpha_1$ and $M\beta_1$ peaks, corroborating the identification. The overlapping of the S $K\alpha_1$ and $K\beta$ peaks with the Hg distribution in the elemental maps provided further data towards the conclusive confirmation of the mercuric sulphide compounds. Vermilion is observed in many red layers, often mixed as a minor component within an amorphous red-ochre matrix. In those cases, the FORS spectra are mainly dominated by features attributable to red ochres, due to their overwhelming abundance. Elsewhere, such as in the mural painting of the Church of Panagia Kera, in Kritsa, the typical spectral features of vermilion can also be observed due to its more abundant use (Fig. 7).

Under PLM, the vermilion-containing chromatic layers show a bright red–orange hue (Fig. 11). The particles exhibit high relief and, in several instances, their original deep-red glow is replaced by a bright-yellow appearance, due to the high refractive index and birefringence effects bringing anomalous interference colours (Eastaugh et al. 2004; Rutherford et al. 2007). In the μ-samples, vermilion particles show variable sizes and morphologies (e.g., large angular particles or finer ones), either as the main component or mixed with other pigments (such as red-ochres and red lead) (Fig. 8, top left and bottom right PLM images). In general, a correlation can be pointed out between the particles' size and hue, with the bigger ones exhibiting a deep-red hue that tends to shift towards an orange tone as the size decreases.

3.2.3. Red lead – Minium

Red lead (lead tetroxide – Pb_3O_4), also known as minium in its natural mineral form, is one of the earliest synthetic pigments, and its use dates back to the 5th century BCE, in China and the Near East (West FitzHugh 1986; Gliozzo and Ionescu 2022). The ancient nomenclature for red lead carries ambiguity, due to this pigment's close association with cinnabar/vermilion and red ochres, and the differing recipes resulting from their combination (Becker 2022). While "minium" and "red lead" are often used interchangeably, the modern nomenclature distinguishes red lead as the synthetic version and minium as its naturally occurring counterpart. Considering the natural rarity of minium, Pb-bearing red pigments in art are generally of artificial origin (Gliozzo and Ionescu 2022). Since antiquity, the use of red lead alone or in conjunction with vermilion has been a common practice, and the pigment appears in medieval artworks and later in Byzantine manuscripts from the seventh century onwards.

Lead tetroxide particles create a dense and fine textured pigment

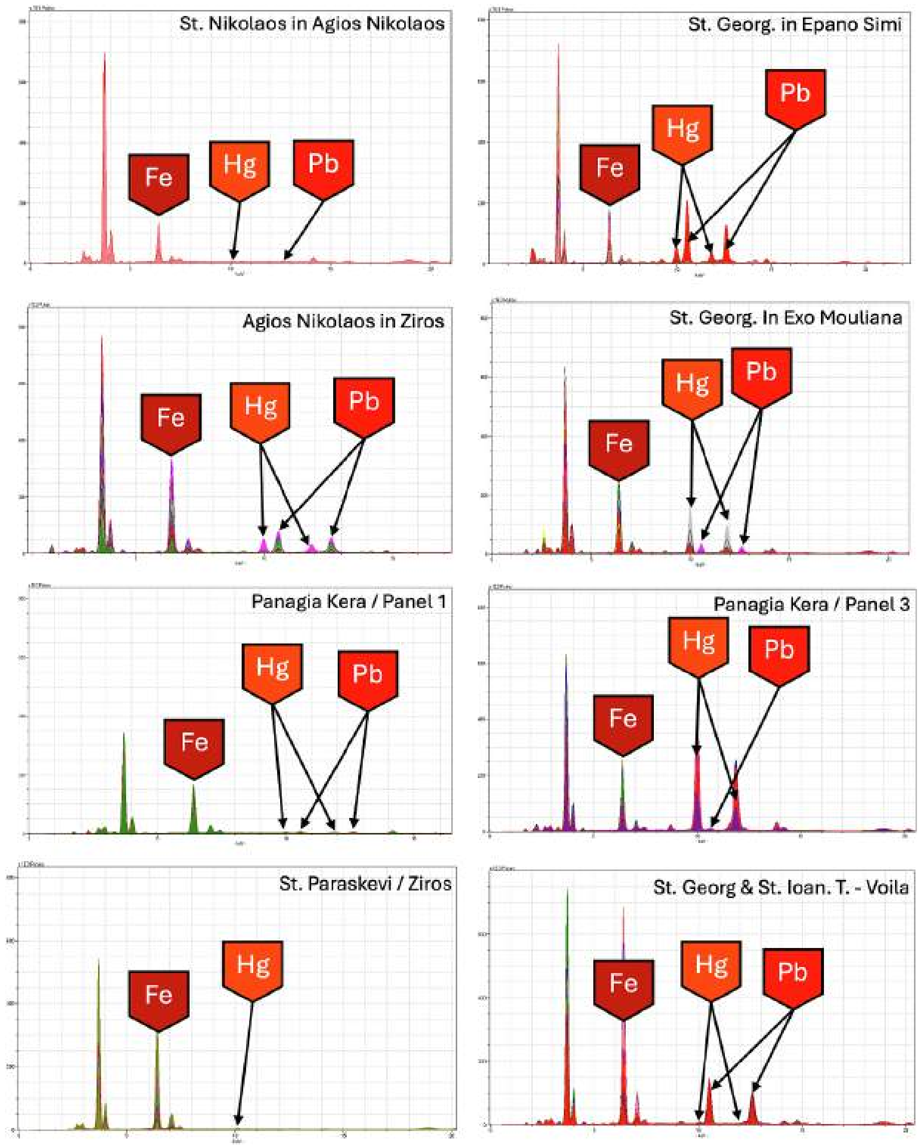

Fig. 6. Representative pXRF spectra of red surface areas from six churches in Crete (labeled). Each spectrum consolidates measurements taken from multiple sampling points within a given site, reflecting the layered stratigraphy of the mural paintings and the frequent co-occurrence of iron ochres, vermilion, and red lead as superimposed layers or mixtures. Ca peaks reflect contributions from both the support layers and lime used as a binder component within the paint matrix (Fig. 8 for the SEM-EDS Ca maps).

with a slight orange hue (West FitzHugh 1986). In its powdered form, red lead resembles the morphology and texture of amorphous red-ochres. In this view, red lead often appears in pigment mixtures alongside ochres, or as an adulteration of more expensive pigments, such as cinnabar/vermilion.

The presence of Pb-bearing compounds within the chromatic layers was indicated in pXRF spectra by the $L\alpha_1$ and $L\beta_1$ peaks for lead (Pb) – at 10.5 keV and 12.6 keV, respectively. Due to the relative abundance of red-ochres in paint layers, FORS data did not reveal any spectral features associated explicitly with red leads, even in those samples where pXRF data showed the presence of Pb.

Red lead was also detected through the SEM-EDS maps through the characteristic Pb $L\alpha_1$ and $L\beta_1$ peaks at the 10.5 keV and 12.6 keV, respectively. However, the identification of Pb on the overlapping $M\alpha_1$ and $M\beta_1$ peaks was not attempted due to the interference of S $K\alpha_1$ and $K\beta_1$ peaks in the 2.3—–2.4 keV range.

3.2.4. *Other components relating to pigments and technique*

3.2.4.1. *Binder and execution technique.*

SEM-EDS elemental maps showed complex structural features for the painted layers, not identifiable with a single pigment, but rather by mixtures of various pigments and additives. Despite the nature of the supporting substrata and the adopted execution techniques (*a fresco, mezzo fresco, and a secco*), the continuous detection of Ca throughout the cross-sections, including the paint layers, is indicative of its deliberate incorporation into the paint matrix during the painting process. Fig. 8 (SEM-EDS maps of Ca at the bottom row) shows the observed widespread distribution of Ca across the samples, which supports its possible role as a principal component of the binding medium. The amorphous fine grains and bigger pigment crystals are embedded within an inorganic crystalline matrix, composed primarily of Ca and Mg carbonates. Furthermore, μ-XRD data collected on isolated μ-samples of red layers (with no support) were also dominated by calcite peaks. Since EDS detects no Ca in hematite crystals, lime might thus have been added to the mixture as a binder.

This is consistent with textual information and archaeometric data

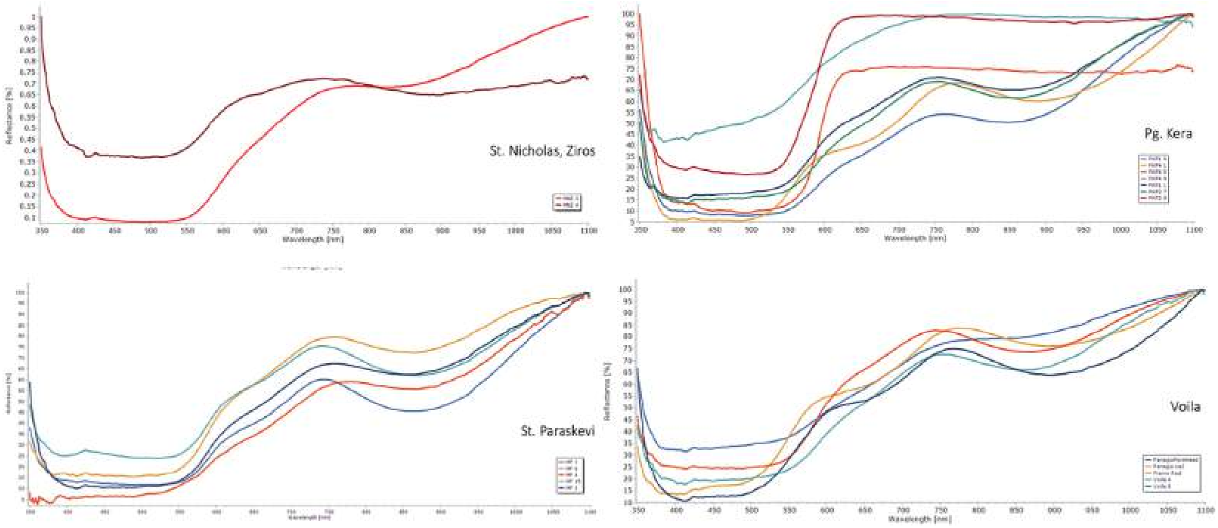

Fig. 7. UV–Vis reflectance (FORS) spectra from churches representing different periods. Top left: Church of St. Nicholas in Ziros, 13th century, where the FORS data from samples showed the characteristic spectral features of red ochres. The same features were apparent for the two 16th century churches of St. Paraskevi and St. George and St. John Theologos. In the church of Panagia Kera in Kritsa, due to the high mercuric sulphide (SEM-EDS) content of the samples, spectral features of vermilion could clearly be captured.

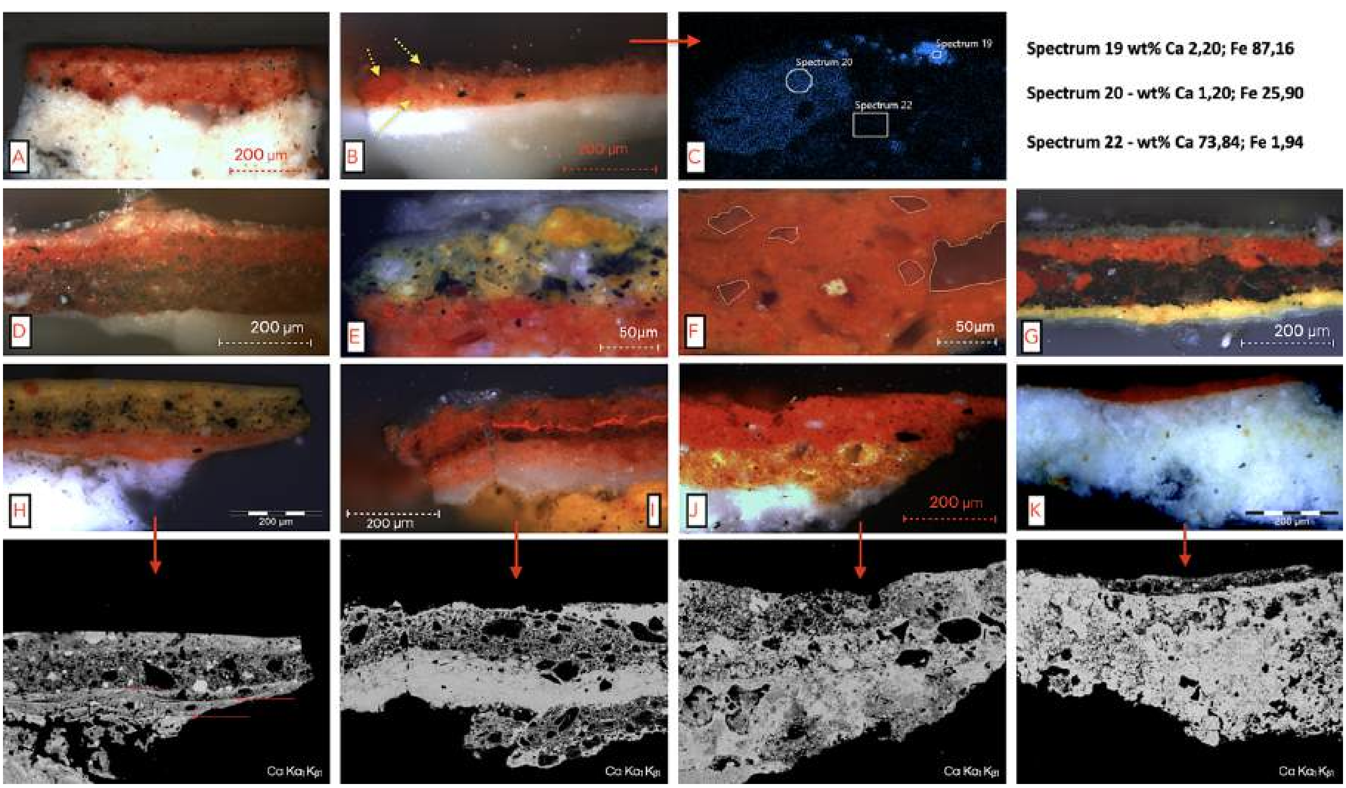

Fig. 8. Comparative PLM images featuring the morphological and optical characteristics of the chromatic layers containing red ochres, vermillion and red lead. The samples from Panagia Kera and Exo Mouliana (Boxes A and B) featuring three different morphologies for the encountered red-ochres: composite multi-grain particles with aluminosilicate inclusions, high Fe hematite particles and the amorphous red-ochre phases embedded in a Ca rich binder matrix. Box C: EDS data relating to the varying chemical composition characteristics of such particles: spectrum 19 hematite crystal; spectrum 20 composite multi grain particle; spectrum 22: amorphous red ochre embedded in a Ca rich matrix. The bottom BSE Ca images show that in addition to the final preparatory layer, the chromatic layers are also featuring Ca content, suggesting the application of the pigments mixed with lime, as a binder component.

on Byzantine mural paintings from other regions and periods, accounting for the common practice of mixing pigments with lime putty before applying them on the painting (Winfield 1968; Thompson 2019; Mastrotheodoros and Beltsios 2022).

3.2.4.2. Carbon black, lime white and other components. The pXRF spectra acquired from black areas were dominated by Ca peaks, often coupled with Cu peaks. These results, combined with the DPOM images of the black surfaces showed irregular, black coloured particles consistent with a C based pigment (Eastaugh et al. 2004). Comparative study

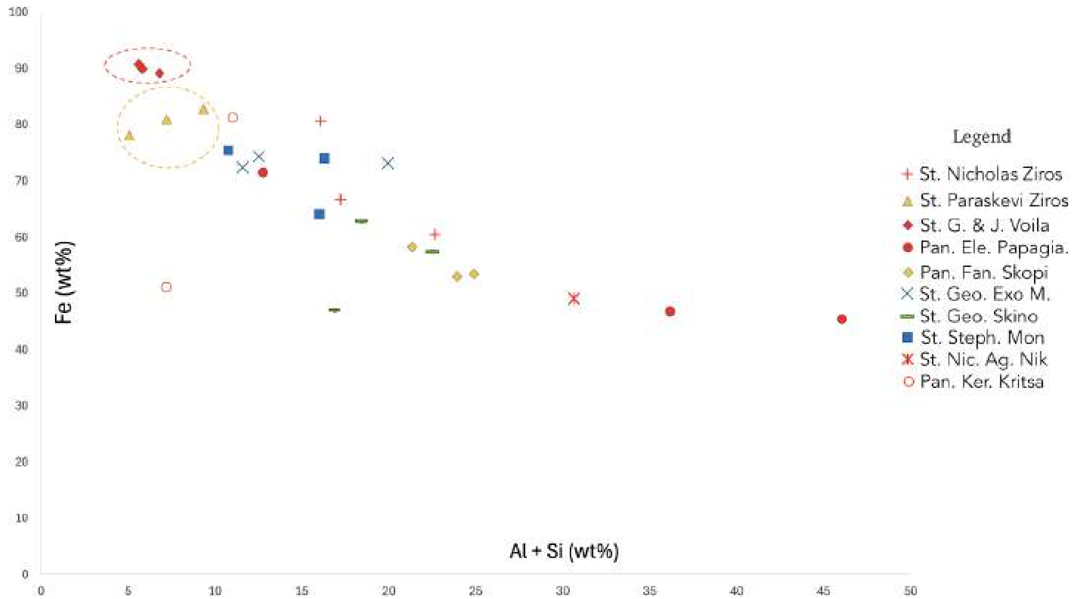

Fig. 9. Scatter plot of Fe (wt%) and Al + Si (wt%) based on SEM-EDS data acquired from hematite particles on red chromatic layers. The distribution data demonstrated the high variability of the Fe vs. Al + Si values, due to the non-homogeneous chemistry and structure of the hematite particles. Trends and observations could be extracted nonetheless, such as the increasing purity of red ochres in the 16th century contexts (circled in red and yellow) and presence of ochres of varying quality within the same painting campaign, indicating the possible use of two different type of ochres.

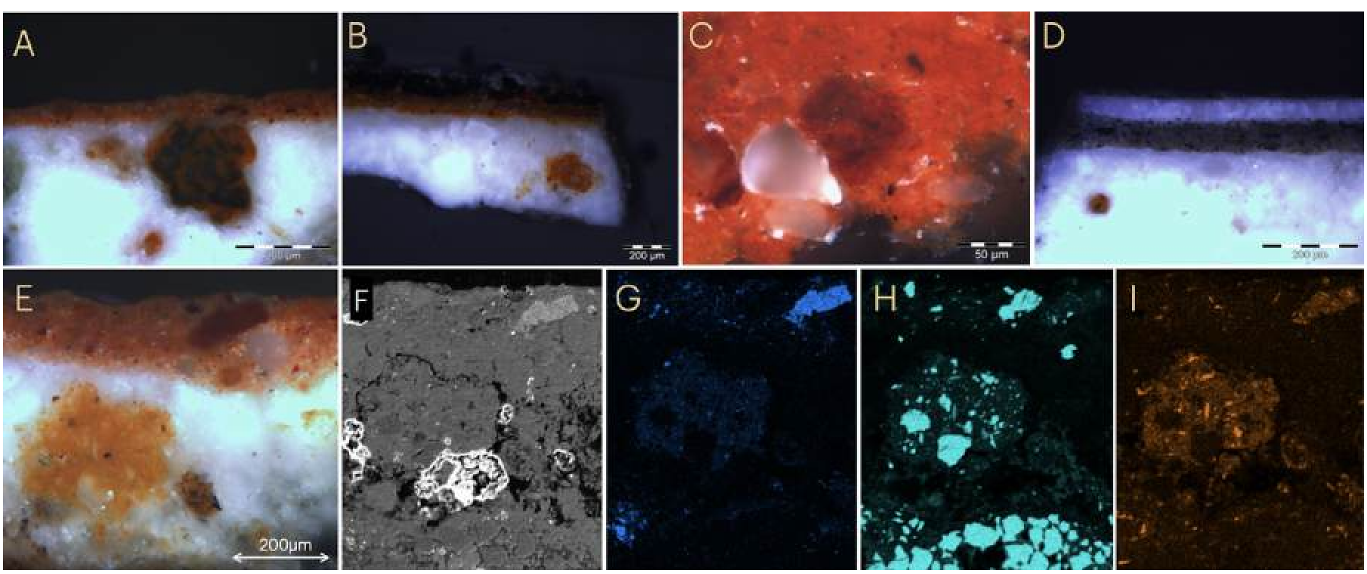

Fig. 10. PLM images of multi – grain ochres. Top row: Church of St. Nicholas in Agios Nikolaos (A), Church of St. Stephen in Monastiraki (B), Church of St. George and St. John Theologos in Voila (C), Church of St. George in Epano Simi (D). The bottom row illustrates another instance from the Church of St. Nicholas in Agios Nikolaos, along with the SEM-BSE image (F), SEM-EDS Fe map (G), Si map (H) and Al map (I).

of the PLM images parallel to SEM-EDS maps of C showed that these irregular zones were composed of C-rich particles, indicative for the use of carbon-black. This occurrence was consistently observed in all the churches where pXRF analysis of the black background surfaces was carried out. In addition, in the churches from the 13th century through 16th century, use of C black as a base layer for enhancing the optical properties of the overlying chromatic stratum was observed.

For the modification of red tones and highlights, a Ca bearing pigment, lime white was identified. This conclusion was supported by the pXRF spectra of white areas, and SEM-EDS data relating to the white highlight layers applied over red tones. In this context, the abundant Ca signal in the pXRF and EDS data and absence of Pb peaks were interpreted as evidence for the use of lime white, a finding consistent with literature (Winfield 1968; Cheilakou et al. 2014; Nicola et al. 2018).

In the microphotographs, angular, light-coloured particles, identified as quartz crystals, were often encountered, embedded in the paint matrix (Fig. 8 Box F, areas circled in white dotted lines). In terms of their morphological features and size, the characteristics of these particles did not concur with the overall pigment morphology, suggesting their function as an additive or modifier.

4. Discussion

4.1. Red ochres, vermilion and red lead

As indicated in the results, in the mural paintings surveyed and

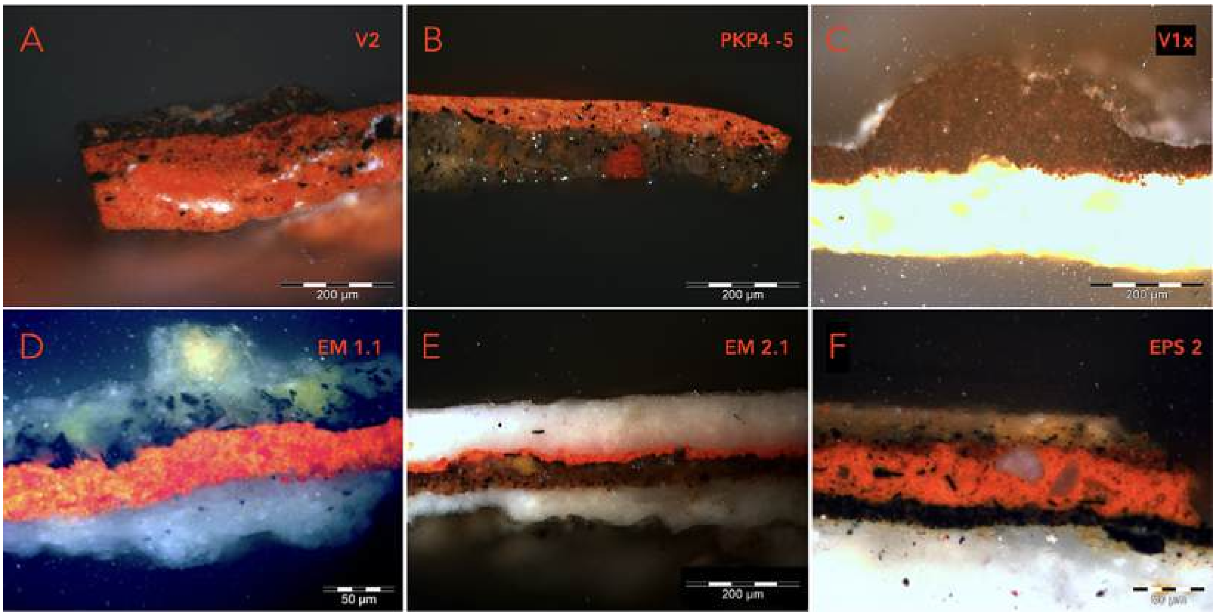

Fig. 11. PLM images of chromatic layers featuring vermillion, red leads, along with C black, red ochres and yellow ochres. Top left: Voila, chromatic layers from the central Mother Mary figure, with the discernible degradation layer of red lead on top, appearing black. Top middle: Church of Panagia Kera in Kritsa, chromatic layer from the garment of Jesus Christ, top layer executed in vermillion and the bottom lower stratum featuring red ochres, red lead and C black. Top right, Voila, degradation of the red lead top layer. Bottom left and center: Church of St. George in Exo Mouliana; use of vermillion as a ground layer. Bottom right: Church of St. George in Epano Simi, use of red ochre and cinnabar as a ground layer for the skin tones.

analysed, for the production of red tones, red ochres, vermilion and red lead were used. SEM-EDS elemental maps further showed complex structural features for the painted layers, not identifiable with a single pigment, but rather by mixtures of various pigments and additives, such as C black and lime white. In effect, while the chromatic palette of reds was limited, the application of the pigments and execution technique of the murals were marked by a high level of diversity across the mural paintings studied. Nevertheless, in terms of the overall effect the characteristic Byzantine style of three-tone system was predominant, through the separation and layered application of different tones of red. This separation of colours and tones is a distinguishing feature of the Byzantine style and contrasts with the blending of colors seen in later times in the West. The predominantly linear appearance resulting from the layered application of distinct tones creates one of the fundamental features of Byzantine wall painting (Fig. 5; Fig. 8, Box D).

In addition to the classification of hematite crystals according to their morphological characteristics and their purity in terms of Fe percentages, the compositional diversity of the grains provided further opportunities for comparing the characteristics of hematite in the mural paintings analysed. Natural forms of hematite do not come as pure Fe-bearing phases and always consist of other accessory elements due to their geological formation processes, resulting in the inclusion of accessory minerals such as Al and Si. In this view, the compositional variations resulting from the variable Fe versus Al + Si ratios allow the comparison of hematite grains from the samples included in this study (Fig. 9).

In this context, the EDS point analyses of μ-samples from two 16^{th}-century churches (St. Paraskevi in Ziros and St. George and St. John Theologos in Voila) revealed the consistent use of higher purity red ochres with hematite Fe concentrations over 80 wt%. The differences in the combined Al + Si values of these pigments from these churches point to the different preparation processes and sources. Namely, in Voila, the red ochres were relatively purer, with high Fe hematites featuring lower levels of accessory aluminosilicate components. Furthermore, in terms of purity, the EDS data from Voila confirmed the presence of at least two different types of red ochres, with the first type featuring a lower Fe content (Fe 46.0 wt%; Al 9.0 wt%; Si 16.4 wt%) and the second and purer type featuring higher Fe concentration (Fe 90.0 wt%; Al 1.4 wt%; Si 4.6 wt%).

The presence of the multi-grain ochre particles could be related to the use of ochres in Byzantine preparatory drawings. One of the defining characteristics of preparatory drawings is the frequent alterations and modifications within the sketches themselves (Winfield 1968). Presumably, the painters often composed their scenes directly on the wall as the painting progressed, rather than completely adhering to a pre-determined model or drawing. In this view, the presence of these grains could (non-exhaustively) be explained through such alterations that resulted in the entrapment of a grain in the newly modified support layer. Similar ochre particles were previously reported in paintings from post-Byzantine icon paintings from Epirus, Greece (Mastrotheodoros 2018) and identified as Mn containing Fe occurrences common to the area. On the other hand, while similar in morphology, the EDS data from the Church of St. Paraskevi yields a slightly different elemental profile to the Epirus samples, richer in K rather than Mn.

The almost systematic presence of the quartz crystals embedded in several ochre matrices led us to suppose that they might have been deliberately added to the pigment admixture, to facilitate grinding, to aptly reach the proper grain size (and, consequently, the desired shade of red). Quartz, in fact, is considerably harder (H = 7 in the Mohs scale) than hematite (H = 5–6) and clay minerals (H = 2–3) and as such it may favour grinding of the red particles to the desired size (Best et al. 1992; Rosalie David et al. 2001; Mastrotheodoros and Beltsios 2022). However, the possibility that these quartz crystals represent original contamination of the raw pigment cannot be ruled out (Helwig 2007).

It is often highlighted that both the natural and synthetic forms of mercuric sulphide pigments were considered as valuable and expensive materials since antiquity (Kakoulli et al. 2012; Bakiler et al. 2016; Thompson 2019). In this perspective, previous studies on Byzantine mural paintings frequently highlight the special role reserved to this pigment for painting prominent figures, focal points and important decorative elements. In the analysed mural paintings, however, PLM and SEM-EDS maps show that vermilion is a consistent component of the red areas and used in a variety of roles. For example, it could represent either the main pigment within the stratigraphic succession or a minor component within an amorphous red-ochre matrix, in some cases in combination with red lead. Instances where vermilion represents the main pigment are likely to be tied to the Byzantine three-tone system, in which this precious and bright material was typically reserved for the final (uppermost) chromatic layer. Its abundance, albeit with significant variation in different areas, suggests that vermilion was considered an essential ingredient of the paint recipes for reds. This assumption is further supported by its detection in less significant areas – such as border frames and underlying red layers – implying a relatively constant use.

The diachronic consideration of vermilion's use and abundance in the mural paintings of the Lassithi region did not reveal any consistent correlation or trend. Vermilion frequently appears in mural paintings, as evidenced by its use in the Church of St. Nicholas in Ziros. In this context, while this pigment features as a component of the red tones, its use is limited to the relatively significant aspects and focal points of the painting. Later periods see the use of vermilion for ground layers of garments, skin tones, and other elements (Fig. 11 PLM images EM1.1, EM2.1 and EPS 2). Another instance of the variable use of vermilion is evident in the two contemporaneous 16^{th} century churches located in close proximity (near Handras – Voila and Ziros) – i.e., those of St. George and St. John Theologos in Voila and St. Paraskevi in Ziros) – clearly show different approaches in the use of vermilion. In the former, vermilion is sparingly used for enriching the quality and brilliance of reds. In the latter, instead, this pigment is used in large areas of the painting, including the borders, reflecting a differing approach in the more generous investment of materials and artistic complexity.

As indicated in the literature, the low stability of vermilion (related to the behaviour of sulfur and sulfur-driven degradation mechanisms) can be mitigated by the application of iron-oxide pigments (i.e. red-ochres) as buffering sub-layers. Iron-oxide compounds are generally considered highly stable compounds and often have a stabilising effect in the paint matrix (Pfaff 2017). In this and other contexts (Argote et al. 2020), the use of iron-oxide pigments beneath the mercuric sulfide also served, besides the technical and visual aims of the painter, as a barrier between the vermilion and the alkaline $CaCO_3$ ground layer, exerting a protective function.

The use of red lead was relatively limited, and it was generally used as an additive to red ochres and vermilion, except for the Church of St. George and St. John Theologos in Voila where highlights of central figures were executed through the ample use of red leads. On SEM-EDS and PLM data, the close association of the red lead bearing paint layers with those containing vermilion was often encountered, suggesting a vermilion – red lead mixture, parallel to textual sources and case studies on Byzantine mural painting (West FitzHugh 1986; Cheilakou et al. 2014; Demir et al. 2018; Thompson 2019; Fioretti et al. 2023). In addition, recent analyses also confirm that red lead was frequently used in the Byzantine context for the modification of red hues, appearing in icons painted in the Cretan style (some of which are attributed to prominent Cretan painters) and in multi-pictorial phase wall paintings in northern Greece, Cyprus, and Bari, Italy (Pelosi 2013; Armetta et al. 2021; Malletzidou et al. 2021; Stamboliyska et al. 2021).

The SmART_scan maps provided further opportunities for a comparative spatial visualization of the pigments across the mural paintings. In the cases when the pigments were used as a mixture intentionally, variations of their intensities in the elemental maps provided indications, though non quantitatively, into the proportions and locations of these mixtures. For instance, in the case of the church of St. Nicholas in Ziros (13^{th} century), vermilion was visualized in extensive areas of the painting, but the use of red lead appeared more restricted. Both red lead and vermilion were detected within the border frames, indicating their widespread use along with red ochres, as previously noted (Fig. 12).

Similarly, Cu distribution maps within the black regions of the paintings point out that, consistent with prior literature (Winfield 1968), Cu based blue pigments can be encountered mixed with C black, where this black-blue mixture was often applied as a primary background underlayer before the execution of other components of the painting. This interpretation is further supported by the frequent detection of Cu under the haloes and figures, demonstrating that the Cu containing base layers were present under these layers as well (Fig. 12, SmArt Scan Cu map (right)).

4.2. Colour changes

4.2.1. Thermal degradation of red ochres

During the field surveys and in-situ analyses of the mural paintings, several anomalies were observed that involve red pigments. A typical one is the systematic presence, in some yellowish and green areas, of circumscribed red spots typically appearing as vertical rectangular shapes with pointed upper edges, apparently unrelated to the original composition and colour scheme of the paintings. Macro-VIS photography and digital portable optical microscopy provide higher resolution imaging of a possible pigment transformation process, responsible for turning yellow and green areas into distinct spots of red. This transformation is further visible at the PLM – e.g., in the μ-sample obtained from the Church of Panagia Kera in Kritsa, where the presence of both an unaltered yellow layer and transformed red spots is visible. In-situ elemental analyses performed on these spots revealed a consistent presence of Fe (Kα1 and Kβ1 peaks at 6.4 keV and 7.0 keV, respectively).

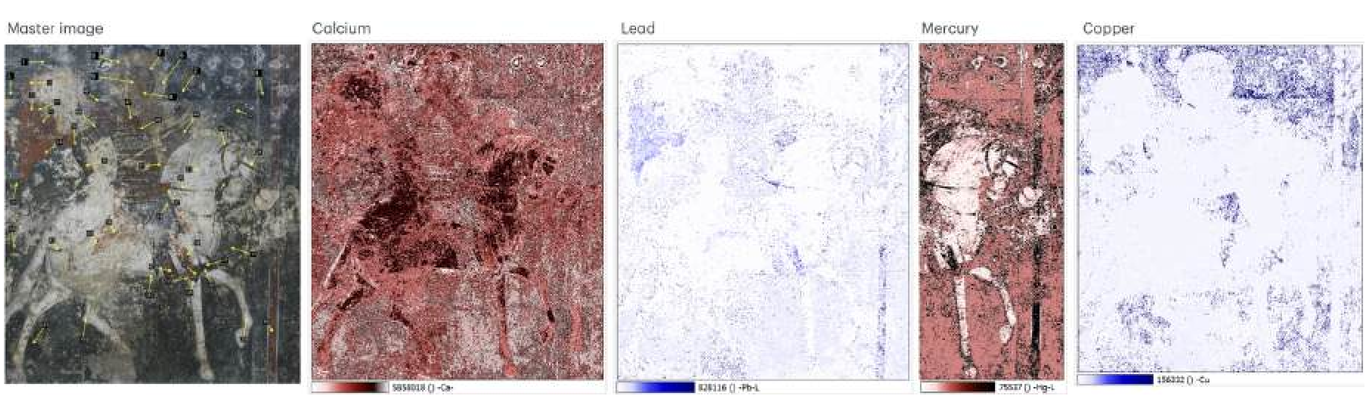

Fig. 12. False-colour composition (FCC) maps of the main panel from the Church of St. Nicholas in Ziros (13^{th} century). From left to right: Master image of the panel in visible light (image credit. Y.Z. Helvacı); FCC map for Ca, with the higher intensity areas highlighted in dark red to black; FCC map for Pb for the visualization of red lead use across the painting. Please note the border frame in red, containing red lead within the mixture, along with vermilion; FCC map for Hg and the spatial distribution of vermilion across the painting; FCC map for Cu, demonstrating its spread across the black areas, highlighting the use of a Cu based blue pigment in combination with C blacks. (FCC maps: Giacomo Chiari).

Based on the color information and chemistry (pXRF and SEM-EDS maps), the original pigment can be identified as yellow ochre (goethite α-FeO(OH)). The primary mechanism behind this transformation (and turning to a red hue) could be thermal degradation, which is known to cause loss of the water/hydroxyl component (OH/ H_2O) from Fe-oxide hydroxide particles (goethite) when they are exposed to heat, converting them into anhydrous Fe-oxide components (hematite).

Both the shape and circumscribed position of these red spots indicate that they could have been caused by the positioning of candles during ceremonies close to the wall painting surfaces, which could have induced enough thermal stress to trigger such a transformation. The heating of yellow ochres and their consequent transformation to red ones is well documented in literature – e.g., at Herculaneum (Helwig 2007; S. Sotiropoulou et al. 2008; Iordanidis et al. 2011; Secco et al. 2021). Further confirmation about this transformation here is provided by PLM analysis, where particles belonging to various stages of the goethite-to-hematite conversion are visible within the same sample (Fig. 13).

Notably, this phenomenon offers further information about the execution techniques employed. In several churches (e.g., St. Nicholas in Ziros and Panagia Eleousa in Papagiannades), extensive green background areas were obtained through a substrate of yellow ochres topped by a surface layer of C black. This layering technique is also observed in other Byzantine contexts and used to produce a dark-green optical effect due to the subtractive mixing of the pigments (Daniilia et al. 2008; Alberghina et al. 2024; Cortea et al. 2024). In those areas where thermal degradation occurs, the yellow ochre substrate is transformed into red ochre, disrupting the original blending, and the overlying black hue no longer yields a green effect.

4.2.2. Chromatic alteration of lead red and vermilion

Further instances of chromatic alteration of red surface areas were documented. In the 15th-century church of St. George in Epano Simi (Hierapetra), the chromatic layers of the central aisle at the upper vault section showed different types of degradation processes, such as the erosion of black chromatic layers and darkening of red areas. In what concerns the red areas, particularly in the depiction of Christ Healing the Blind scene on the same panel, the highlights of the garment of the blind figure appear black. The pXRF spectra of the unaltered mid–tone red areas were characterised by Fe peaks, indicative of red ochres. On the other hand, both the bright red highlight areas and the now-darkened highlights exhibited Fe peaks along with Hg and Pb Lα and Lβ peaks. This combination was indicative of the use of a mixture consisting of vermilion (HgS) and red lead. The observed darkening of these layers is likely related to degradation mechanisms of vermilion and red lead, resulting from excessive humidity and water infiltration problems within the support structure (S. Sotiropoulou et al. 2008; Armetta et al. 2021; Giumlia-Mair et al. 2022; Gliozzo and Ionescu 2022). Comparable pathologies were also observed in the 16th-century church of St. George and St. John Theologos in Voila (Fig. 11, PLM images top left and top right). For instance, the halos of the two angel emblems flanking the central Mother Mary figure were characterised by a dull grey surface colour marked by weak Ca and Fe peaks in pXRF measurements, which at the same time showed prominent Pb Lα and Lβ peaks. Given that Pb peaks were also present in other parts of the painting (in combination with Hg and Fe), the presence of red lead, though in degraded form, was considered the most likely scenario for such dull grey areas.

Furthermore, in Voila, the μ-samples obtained from the highlights of the central Mother Mary figure's face revealed similar findings under PLM, where a degraded chromatic layer of red lead was observed. This dense and fine-grained dark chromatic layer assumed a brownish-red appearance when the illumination intensity was increased under PLM. The Pb distribution data obtained through the SEM-EDS analysis further confirmed the presence of red lead, whose chromatic degradation resulted in the visible dull grey appearance (Fig. 11, Box C, V1x).

The findings outlined above indicate that red leads were utilised diversely for the execution of different visual elements of mural paintings. At the same time, these pigments appear to have undergone degradation processes, resulting in chromatic alterations, which compromise the visual integrity of the mural paintings over time. These alterations are consistent with the well-documented propensity of red lead for chromatic alterations and darkening in wall paintings and other media (West FitzHugh 1986; Nöller 2015; Pfaff 2017; Thompson 2019).

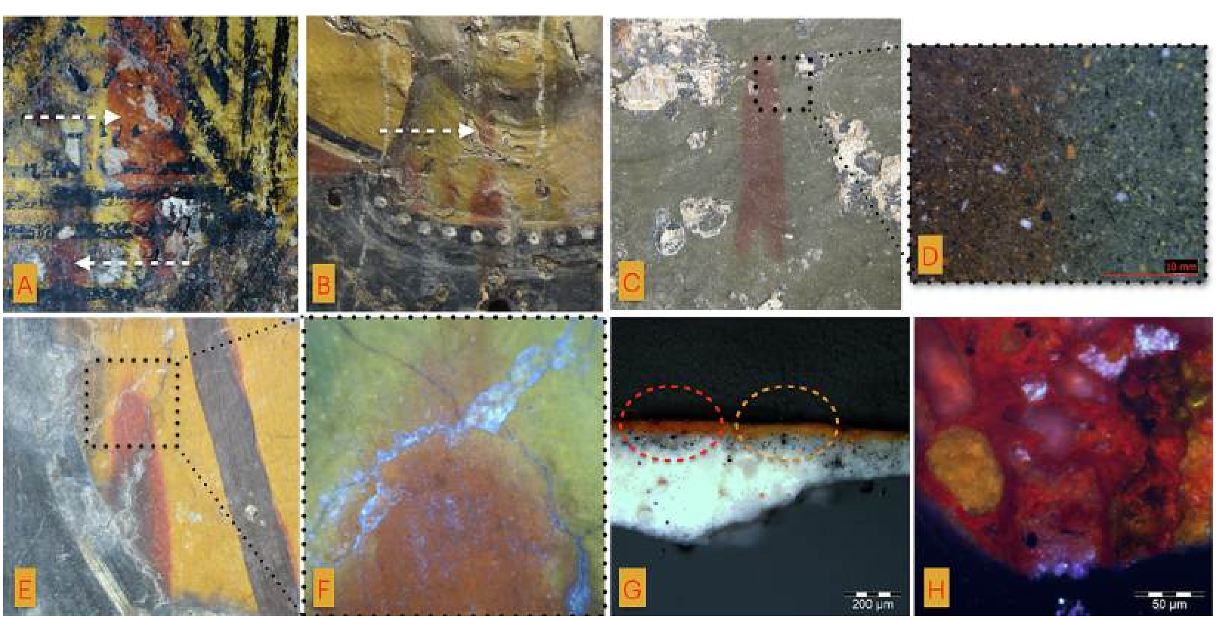

Fig. 13. Thermal degradation of yellow ochres through the goethite – hematite transformation, as a result of the loss of the water/hydroxyl component. The boxes A (Church of Panagia Faneromeni in Skopi) B (Church of St. George in Exo Mouliana), C and E (Church of St. Nicholas in Ziros) demonstrate the various instances of this occurrence. Box D and F, magnified images of C and E, illustrate the different stages of this transformation, with the left side appearing a darker reddish tone and on the right yellow ochre particles clearly visible. In the same image, disappearance of the green hue with the red particles is noted (D). Box G and H, PLM images of the degradation spots, illustrating the presence of the multiple phases that belong to the stages of this transformation.

While the different mechanisms that cause the chromatic alteration of red lead are beyond the scope of this paper, the observations, analyses, and resulting data align with the relevant literature on the instability of Pb–based red pigments.

5. Conclusions

Through a multi-analytical approach consisting of imaging techniques and synergic in-situ and laboratory analyses, the mineral-chemical, micro-structural, and textural features of the red pigments used in wall paintings were determined for eleven churches from eastern Crete, providing a comprehensive diachronic dataset in relation to the Byzantine mural paintings of the region.

In the analysed mural paintings, a relatively restricted palette was employed for reds – namely Fe-oxide (hematite bearing red ochres), vermilion, and red lead. Furthermore, main red tones could be modified through the addition of other pigments, such as yellow ochres, C black, and Ca white.

Red ochres were the most frequently encountered and versatile pigment, and their presence was consistent on the mural paintings from all the periods. They could be classified into three main groups, namely amorphous red ochre matrices with Ca (binder), hematite particles rich in Fe, along with other accessory clay minerals, and the multi-grain ochre particles with varying mineralogical phases and morphological features within a unique particle. The purity levels of red ochres, as a function of their relative Fe versus Al + Si content, were investigated. The collection and statistical treatment of the SEM-EDS data posed challenges due to the highly non-homogeneous nature of the particles from the red ochre group, resulting in variable standard deviation values compared to mean values acquired from the point analyses. On the other hand, the following trends and conclusions could be drawn: Hematites from the 8^{th}-century mural painting in the Church of Agios Nikolaos in the city of Agios Nikolaos were characteristically low in Fe content, suggesting a lower purity. Overall, most of the investigated mural paintings were characterised by hematite particles exhibiting moderate Fe content (Fe > 50 wt% and < 75 wt%). Hematite particles from the two 16^{th}-century churches in Ziros and Voila revealed very high levels of Fe (Fe > 80 wt%), indicating the relatively high quality of the red ochres used in these artworks.

Vermilion is the second most frequent red pigment used; as an expensive material, it was often mixed with lead (which is frequently suggested as adulteration, although its use as a color-modifier cannot be ruled out). After the 14^{th} to 15^{th} centuries, its occurrence in the mural paintings became more frequent; however, its abundance and application vary significantly according to the modus operandi of the artists. This restrained yet deliberate application of vermilion aligns with our understanding of its economic value, while also underscoring its brilliance and significance within the visual language of their paintings.

The application of red pigments followed the three-tone system, typical of Byzantine painting practice. Though the pigment selection was limited, the technical application (i.e., through stratigraphy) revealed a high level of creativity and technical differences in the achievement of desired hues. This is particularly evident in the comparison between the churches of St. Paraskevi in Ziros and St. George and St. John Theologos in Voila (contemporaneous 16^{th} century churches in close geographical proximity), where markedly distinct visual styles and approaches to pigment use were observed, reflecting differences in patronage investment and technique of the painters.

While the presence of organic binders is still not yet conclusively established (though PLM under UV light on cross-sections indicates some fluorescence), XRF, XRD, and SEM-EDS data strongly indicate that the chromatic layers are often dominated by a Ca carbonate matrix, suggesting the intentional use of a lime putty mixed with the pigments. Furthermore, the presence and/or absence of the carbonation lines in churches and mural paintings indicates that the painters did not operate in a strict *a fresco* – *a secco* dichotomy. Still, the application of the pigments and binder properties was adjusted to the necessities of the technique, showing a more sophisticated and diverse approach.

The diachronic consideration of the mural paintings studied reveals a combination of continuity and gradual change. The prevalence of red ochres, the consistent use of lime as a binder, and the adherence to the three-tone application system represent continuous features of the local painting tradition across the full chronological range of the study. On the other hand, the meaningful shifts observed can be summarized as follows: the increasing purity of red ochres over the period suggests access to progressively higher-quality pigments or improved preparation procedures; the more frequent and diverse use of vermilion from the 14^{th} century onwards reflects a greater economic availability and evolving aesthetic intentions; and the observed differences between contemporaneous churches such as those in Voila and Ziros point to the increasing effect of artistic preferences and patronage on material choices. These findings indicate painting practices that were neither static nor strongly open to external influences, but rather practices that evolved organically from within, shaped by the cultural and economic shifts taking place in the region.

In addition to their archaeometric significance, the findings of this study carry direct implications for the conservation and preservation of the mural paintings examined. The documentation and characterisation of pigment degradation phenomena, such as the thermal transformation of yellow ochres to hematite and the chromatic darkening of red lead under humid conditions, provides information regarding the conservation diagnosis of the mural paintings indicated. In particular, the localized red spots observed in yellow and green areas, attributable to candle-induced thermal stress, constitute a diagnosable and potentially ongoing process whose progression could be monitored and mitigated through targeted controls and liturgical practice. Similarly, the identification of lime as a consistent binder component across multiple churches and periods has direct implications for the selection of compatible consolidation and cleaning materials in future interventions, since the alkalinity of lime-based matrices must be accounted for in any treatment protocol. The results and insights provided by this project also establish a material reference dataset for the region of Lassithi, which can facilitate condition assessments and guide strategies in future conservation campaigns.

CRediT authorship contribution statement

Yiğit Zafer Helvacı: Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Roberto Giustetto:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Methodology. **Giacomo Chiari:** Writing – review & editing, Software, Data curation. **Tiziana Cavaleri:** Writing – review & editing, Resources. **Maurizio Aceto:** Writing – review & editing, Resources. **Klio Zervaki:** Writing – review & editing, Resources. **Monica Gulmini:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Methodology, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We would like to thank the Ephorate of Antiquities of Lassithi, Chryssa Sofianou, as well as the Holy Metropolis of Hierapetra and Siteia, His Eminence Metropolitan Kyrillos for their support regarding visits of the monuments presented in this paper. We are also indebted to Patrizia Davit (University of Turin - Chemistry Department), Nadia

Curetti, Davide Bernasconi, Stefano Ghignone and Carmelo Sibio (University of Turin - Department of Earth Sciences) for their assistance during laboratory analyses, Hilal Köksalan (Mimar Sinan Fine Arts University) for her contribution in the architectural survey of the monuments. We also thank Rui Bordalo (Catholic University of Portugal, Porto) for his contribution as an external proofreader, as well as the anonymous reviewers who, with their advice and suggestions, significantly helped to improve the scientific quality of the manuscript.

Funding

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 754511.

References

Aceto, M., Agostino, A., Fenoglio, G., et al., 2014. Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry. Anal. Methods 6 (5), 1488. https://doi.org/10.1039/c3ay41904e.

Alberghina, M.F., Zicarelli, M.A., Randazzo, L., et al., 2024. Byzantine Wall paintings from San Marco d'Aluzio, Sicily: Non-Invasive Diagnostics and Microanalytical Investigation of Pigments and Plasters. Heritage Science 12 (1), 184. https://doi.org/10.1186/s40494-024-01308-z.

Argote, D.L., Torres, G., Hernández-Padrón, G., Ortega, V., López-García, P.A., Castaño, V.M., 2020. Cinnabar, Hematite and Gypsum Presence in Mural paintings in Teotihuacan, Mexico. J. Archaeol. Sci. Rep. 32 (August), 102375. https://doi.org/10.1016/j.jasrep.2020.102375.

Armetta, F., Chirco, G., Celso, F.L., et al., 2021. Sicilian byzantine Icons through the use of Non-Invasive Imaging Techniques and Optical Spectroscopy: the Case of the Madonna Dell'Elemosina. Molecules 26 (24), 7595. https://doi.org/10.3390/molecules26247595.

Bakiler, M., Kırmızı, B., Öztürk, Ö.O., et al., 2016. Material Characterization of the late Roman Wall Painting Samples from Sinop Balatlar Church complex in the Black Sea Region of Turkey. Microchem. J. 126 (May), 263–273. https://doi.org/10.1016/j.microc.2015.11.050.

Becker, H., 2022. Pigment Nomenclature in the Ancient Near East, Greece, and Rome. Archaeol. Anthropol. Sci. 14 (1). https://doi.org/10.1007/s12520-021-01394-1.

Best, S.P., Clark, R.J.H., Withnall, R., 1992. Non-Destructive Pigment Analysis of Artefacts by Raman Microscopy. Endeavour 16 (2), 66–73. https://doi.org/10.1016/0160-9327(92)90004-9.

Bikiaris, D., Sister Daniilia, S., Sotiropoulou, et al., 2000. Ochre-Differentiation through Micro-Raman and Micro-FTIR Spectroscopies: Application on Wall paintings at Meteora and Mount Athos, Greece. Spectrochim. Acta A Mol. Biomol. Spectrosc. 56 (1), 3–18. https://doi.org/10.1016/S1386-1425(99)00134-1.

Bissinger, M., 1995. *Kreta*. Byzantinische Wand-Malereien, Editio Maris.

Caple, C., Williams, E., 2000. *Conservation skills for the 21st Century: Judgement.* Routledge, Method and Decision-Making. Second Edition.

Cennini, C., 2014. *Il Libro Dell'arte, o Trattato Della Pittura.* Edizione Elettronica, Milano.

Cheilakou, E., Troullinos, M., Koui, M., 2014. Identification of Pigments on byzantine Wall paintings from Crete (14th Century AD) using Non-Invasive Fiber Optics Diffuse Reflectance Spectroscopy (FORS). J. Archaeol. Sci. 41 (January), 541–555. https://doi.org/10.1016/j.jas.2013.09.020.

Cormack, R., 2000. *Byzantine Art,* 1st ed. Oxford University Press, Oxford History of Art.

Cortea, I.M., Ghervase, L., Ratoiu, L., Țentea, O., Dinu, M., 2024. New Insights into the Materials and Painting Techniques of Ancient Wall paintings from the Roman Province of Dacia: a Minimally Invasive Multi-Method Approach. Heritage 7 (9), 5268–5294. https://doi.org/10.3390/heritage7090248.

Daniilia, S., Minopoulou, E., Andrikopoulos, K.S., Tsakalof, A., Bairachtari, K., 2008. From byzantine to Post-byzantine Art: the Painting Technique of St Stephen's Wall paintings at Meteora, Greece. J. Archaeol. Sci. 35 (9), 2474–2485. https://doi.org/10.1016/j.jas.2008.03.017.

Demir, S., Şerifaki, K., Böke, H., 2018. Execution Technique and Pigment Characteristics of byzantine Wall paintings of Anaia Church in Western Anatolia. J. Archaeol. Sci. Rep. 17 (February), 39–46. https://doi.org/10.1016/j.jasrep.2017.09.037.

Despotakis, E., Tsamakda, V., 2023. Archival evidence and byzantine Art in Fifteenth-Century venetian Crete. Dumbarton Oaks Papers 77, 245–318.

Dionysius of Fourna, Paul. 1989. Ερμηνεία Της Ζωγραφικής Τέχνης - The "Painter's Manual" of Dionysius of Fourna. Translated by Paul Hetherington. Oakwood Publications.

Eastaugh, N., Walsh, V., Chaplin, T., 2004. and Ruth Siddall, eds. Pigment Compendium, A Dictionary of Historical Pigments. Elsevier.

Elias, M., Chartier, C., Prévot, G., Garay, H., Vignaud, C., 2006. The Colour of Ochres Explained by their Composition. Mater. Sci. Eng. B 127 (1), 70–80. https://doi.org/10.1016/j.mseb.2005.09.061.

Fioretti, G., Tempesta, G., Capotorto, S., Eramo, G., 2023. Non-Invasive Characterisation of the Wall paintings in the byzantine Church of Palazzo Simi (Bari, Italy) and Digital Photogrammetric Survey for a Pigment Mapping. Coatings 13 (6), 996. https://doi.org/10.3390/coatings13060996.

Gediminskaite, G., 2019. Foundations of Two-Aisled Churches and the Kallergis Family. Università Ca'Foscari Venezia.

Gerola, Guiseppe. 1917. *I Monumenti Veneti Dell'Isola Di Creta*. R. Instituto Veneto di Scienze, Lettere ed Arti.

Giumlia-Mair, A.R.G., Sedov, V.V., Vdovichenko, M.V., Riccardi, M.P., 2022. On Blue and Green Pigments from the St. George Cathedral of Veliky Novgorod. Adv. Archaeomater. 3 (2), 109–119. https://doi.org/10.1016/j.aia.2023.06.001.

Gliozzo, E., 2021. Pigments — Mercury-based Red (Cinnabar-Vermilion) and White (Calomel) and their Degradation Products. Archaeol. Anthropol. Sci. 13 (11). https://doi.org/10.1007/s12520-021-01402-4.

Gliozzo, E., Ionescu, C., 2022. *Pigments—Lead-based Whites, Reds, Yellows and Oranges and their Alteration Phases*. Archaeol. Anthropol. Sci. 14, 77.

Gombrich, E.H., 1951. *The Story of Art.* Phaidon Publishers Inc.

Google LLC. 2025. Google Earth Pro. V. 7.3.6.10201 (64-bit). Released September.

Helwig, Kate. 2007. "Iron Oxide Pigments: Natural and Synthetic." In *Artists Pigments*, edited by Robert L. Feller, vol. 4. Artists Pigments. Archetype Publications Ltd. & Washington National Gallery of Art.

Hradil, D., Grygar, T., Hradilová, J., Bezdička, P., 2003. Clay and Iron Oxide Pigments in the history of Painting. Appl. Clay Sci. 22 (5), 223–236. https://doi.org/10.1016/S0169-1317(03)00076-0.

Iordanidis, A., Garcia-Guinea, J., Strati, A., Gkimourtzina, A., Papoulidou, A., 2011. Byzantine Wall paintings from Kastoria, Northern Greece: Spectroscopic Study of Pigments and Efflorescing Salts. Spectrochim. Acta A Mol. Biomol. Spectrosc. 78 (2), 874–887. https://doi.org/10.1016/j.saa.2010.12.055.

James, L., 2003. Color and Meaning in Byzantium. Journal of Early Christian Studies 11 (2), 223–233. https://doi.org/10.1353/earl.2003.0027.

Jeffreys, E., Haldon, J.F., Cormack, R. (Eds.), 2008. *The Oxford Handbook of Byzantine Studies.* Oxford Handbooks, Oxford University Press.

Kakoulli, I., Schilling, M., Mazurek, J., 2012. The Murals of the Panagia Phorbiotissa: a Technical Examination. *Asinou across Time: Studies in the Architecture and Murals of the Panagia Phorbiotissa.* Dumbarton Oaks Research Library and Collection, Cyprus.

Kalokyris, Konstantin. 1957. *ΑΙ ΒΥΖΑΝΤΙΝΑΙ ΤΟΙΧΟΓΡΑΦΙΑΙ ΤΗΣ ΚΡΗΤΗΣ The Byzantine Wall Paintings of Crete*. English Edition (1973). Red Dust.

Klontza, V., 2008. Blown Glass in Wall paintings from Kritsa, Crete: a Preliminary Report. Journal of Glass Studies 50, 311–335.

Lymberopoulou, Angeliki. 2016a. Byzantine Art and Renaissance Europe. 1st ed. Routledge. Doi: 10.4324/9781315261041.

Lymberopoulou, A., 2016b. Regional byzantine Monumental Art from venetian Crete. In: Lymberopoulou, A., Duits, R. (Eds.), *Byzantine Art and Renaissance Europe*. Taylor & Francis.

Lymberopoulou, A., 2023. Post-byzantine Cretan Icon Painting: demand and Supply Revisited. Arts 12 (4), 139. https://doi.org/10.3390/arts12040139.

Mafredas, T., Kouloumpi, E., Boyatzis, S.C., 2021. Did Dionysius of Fourna follow the Material Recipes Described in his own Treatise? a first Analytical Investigation of four of his Panel paintings. Heritage 4 (4), 3770–3789. https://doi.org/10.3390/heritage4040207.

Malletzidou, L., Zorba, T.T., Kyranoudi, M., et al., 2021. The Dome of Rotunda in Thessaloniki: Investigation of a Multi-Pictorial phase Wall Painting through Analytical Methods. Spectrochim. Acta A Mol. Biomol. Spectrosc. 262 (December), 120101. https://doi.org/10.1016/j.saa.2021.120101.

Marković, Miodrag. 2016. "Painters in the Late Byzantine World (1204-1453), Monumental Painting in Byzantium and Beyond: New Perspectives." *Painters in the Late Byzantine World (1204-1453), Monumental Painting in Byzantium and Beyond: New Perspectives.*, 1–8.

Martin-Ramos, J.D., Chiari, G., 2019. SmART_scan: a Method to produce Composition Maps using any Elemental, Molecular and image Data. J. Cult. Herit. 39 (September), 260–269. https://doi.org/10.1016/j.culher.2019.04.003.

Mastrotheodoros, G.P., 2018. Probing the Birthplace of the 'Epirus School' of Painting: Analytical Investigation of the Filanthropinon Monastery Murals—Part I: Pigments. Archaeol. Anthropol. Sci. 11, 2821–2836.

Mastrotheodoros, G.P., Beltsios, K.G., 2022. Pigments—Iron-based Red, Yellow, and Brown Ochres. Archaeol. Anthropol. Sci. 14 (2), 35. https://doi.org/10.1007/s12520-021-01482-2.

Mastrotheodoros, G.P., Theodosis, M., Filippaki, E., Beltsios, K.G., 2020. By the Hand of Angelos? Analytical Investigation of a Remarkable 15th Century Cretan Icon. Heritage 3 (4), 1360–1372. https://doi.org/10.3390/heritage3040075.

Miller, P.C., 2000. 'The Little Blue Flower is Red': Relics and the Poetizing of the Body. Journal of Early Christian Studies 8 (2), 213–236. https://doi.org/10.1353/earl.2000.0030.

Mora, P., Mora, L., Philippot, P., 1984. *Conservation of Wall paintings.* Butterworths Series in Conservation and Museology. Butterworths.

Mylopotamitaki, K.K., 2005. *The Church of our Lady at Kritsa.* Heraklion.

Nicola, M., Aceto, M., Gheroldi, V., Gobetto, R., Chiari, G., 2018. Egyptian Blue in the Castelseprio Mural Painting Cycle. Imaging and evidence of a Non-Traditional Manufacture. J. Archaeol. Sci. Rep. 19 (June), 465–475. https://doi.org/10.1016/j.jasrep.2018.03.031.

Nöller, R., 2015. Cinnabar Reviewed: Characterization of the Red Pigment and its Reactions. Stud. Conserv. 60 (2), 79–87. https://doi.org/10.1179/2047058413y.0000000089.

Oriols, N., Salvadó, N., Pradell, T., Jiménez, N., Juanhuix, J., Butí, S., 2023. The Three-Tone System in Sant Climent de Taüll Wall paintings: an Imprint of medieval Treatises. J. Cult. Herit. 62 (July), 114–123. https://doi.org/10.1016/j.culher.2023.05.021.

Patedakis, Manolis S. 2015. "Επιτύμβιο Επίγραμμα Και Παραστάσεις Στη Βόιλα Σητείας: Συμβατικό ή Πραγματικό Μοιρολόι." In *Τα Κρητικά Μοιρολόγια. Μνήμη Σήφη Κοσόγλου, Χρίστου Μακρή Και Οδυσσέα Τσαγκαράκη*, edited by K. D. Moutzoris.

Pelosi, C., Agresti, G., Andaloro, M., Baraldi, P., Pogliani, P., Santamaria, 2013. The Rock Hewn Wall paintings in Cappadocia (Turkey). Characterization of the Constituent Materials and a Chronological Overview. E-Preservation Science 10, 9–108.

Pfaff, G., 2017. *Inorganic Pigments*. De Gruyter.

Picollo, M., Bacci, M., Casini, A., et al., 2002. Fiber Optics Reflectance Spectroscopy: a Non-Destructive Technique for the Analysis of Works of Art. In: Martellucci, S., Chester, A.N., Mignani, A.G. (Eds.), *Optical Sensors and Microsystems*. Kluwer Academic Publishers. https://doi.org/10.1007/0-306-47099-3_23.

Popelka-Filcoff, R.S., Zipkin, A.M., 2022. The Archaeometry of Ochre Sensu Lato: a Review. J. Archaeol. Sci. 137 (January), 105530. https://doi.org/10.1016/j.jas.2021.105530.

Rosalie David, A., Edwards, H.G.M., Farwell, D.W., De Faria, D.L.A., 2001. Raman Spectroscopic Analysis of Ancient Egyptian Pigments. Archaeometry 43 (4), 461–473. https://doi.org/10.1111/1475-4754.00029.

Rutherford, J. Gettens, Robert L. Feller, and W. T. Chase. 2007. "Vermillion and Cinnabar." In *Artistś Pigments*, edited by Roy Ashok, vol. 2. Artists Pigments. Archetype Publications Ltd. & Washington National Gallery of Art.

Sandu, I.C., Anca, S.S., Magrini, D., Bracci, S., Roque, C.A., 2012. Cross-Section and Staining-based Techniques for investigating Organic Materials in Painted and Polychrome Works of Art: a Review. Microsc. Microanal. 18 (4), 860–875. https://doi.org/10.1017/S1431927612000554.

Secco, M., Rainer, L., Graves, K., 2021. Ochre-based Pigments in the Tablinum of the House of the Bicentenary (Herculaneum, Italy) between Decorative Technology and Natural disasters. Minerals 11, 67–97.

Sotiropoulou, S., Sister Daniilia, C., Miliani, F., Rosi, L.C., Papanikola-Bakirtzis, D., 2008. Microanalytical Investigation of Degradation Issues in byzantine Wall paintings. Appl. Phys. A 92 (1), 143–150. https://doi.org/10.1007/s00339-008-4465-7.

Sotiropoulou, S., Daniilia, S., 2010. Material Aspects of Icons. a Review on Physicochemical Studies of Greek Icons. Acc. Chem. Res. 43 (6), 877–887. https://doi.org/10.1021/ar1000082.

Spatharakis, I., 2001. *Dated byzantine Wall paintings of Crete*. Alexandros Press.

Stamboliyska, B., Tapanov, S., Velcheva, E., et al., 2021. The Altar Wall paintings of the Catholicon 'the Nativity of the Virgin', Rila Monastery, Bulgaria: Identification of the Painting Materials by Means of Vibrational Spectroscopic Techniques Complemented by EDX, XRD and TGA Analysis. Spectrochim. Acta A Mol. Biomol. Spectrosc. 247 (February), 119087. https://doi.org/10.1016/j.saa.2020.119087.

Thompson, D.V., 2019. *The Materials of medieval Painting*. Martino Fine Books.

Thompson Jr., Daniel V., 2020. *The Practice of Tempera Painting: Materials and Methods*. Dover Publications.

Trinquier, J., 2013. Cinnabaris et « sang-dragon » : le « cinabre » des Anciens entre minéral, végétal et animal. Revue Archéologique N° 56 (2), 305–346. https://doi.org/10.3917/arch.132.0305.

Tsang, J.-S., Friedberg, E., Lam, T., 2019. An Easy-to-Use Method for Preparing Paint Cross Sections. J. Am. Inst. Conserv. 58 (3), 123–131. https://doi.org/10.1080/01971360.2018.1564198.

West FitzHugh, Elisabeth. 1986. "Red Lead and Minium." In *Artistś Pigments*, edited by Robert L. Feller, vol. 1. Artists Pigments. National Gallery of Art, Washington, Archetype Publications, London.

Westlake, P., Siozos, P., Philippidis, A., et al., 2012. Studying Pigments on Painted plaster in Minoan, Roman and Early byzantine Crete. a Multi-Analytical Technique Approach. Anal. Bioanal. Chem. 402 (4), 1413–1432. https://doi.org/10.1007/s00216-011-5281-z.

Weyer, A., Picazo, P.R., Pop, D. (Eds.), 2015. EwaGlos - European Illustrated Glossary of Conservation Terms for Wall Paintings and Architectural Surfaces, Vol. 17. SERIES OF PUBLICATIONS BY THE HORNEMANN INSTITUTE, Michael Imhof Verlag http://openarchive.icomos.org/id/eprint/1706/.

Winfield, D.C., 1968. Middle and later byzantine Wall Painting Methods. a Comparative Study. Dumbarton Oaks Papers 22, 61. https://doi.org/10.2307/1291276.

Wreschner, E.E., Bolton, R., Butzer, K.W., et al., 1980. Red Ochre and Human Evolution: a Case for Discussion [and comments and Reply]. Curr. Anthropol. 21 (5), 631–644. https://doi.org/10.1086/202541.