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Case study

Non-invasive study of Early Medieval wall paintings in the churches of St. Stephan in Chur and St. Martin in Disentis (Switzerland)

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A B S T R A C T

The Early Medieval wall paintings preserved in historical sites of the ancient *Raetia Curiensis* region (today's Swiss Canton of Grisons and parts of Northern Italy and Austria) provide a rare testimony of the art of this period.

This contribution presents the results of the non-invasive scientific campaigns carried out in the churches of St. Stephan in Chur and St. Martin in Disentis/Mustér (Canton of Grisons, Switzerland). In the church of St. Stephan, the investigations were performed *in-situ* on the surviving wall paintings of the crypt and on several painted plaster fragments (crypt and upper church), while in Disentis a selection of painted stucco fragments was studied. All the painted surfaces were firstly examined with technical photography in visible, infrared, and ultraviolet ranges, followed by portable spectroscopic point analyses (i.e. HH-XRF, FORS, and FTIR). The findings revealed the composition of most pigments such as iron-based pigments (yellow and red ochres, green earth) and lead-based pigments (i.e., lead white and red lead). In addition, for the St. Stephan's site, the Visible Induced IR Luminescence (VIL) images combined with point analyses, allowed for the identification of Egyptian blue (EB). Furthermore, the presence of zinc in the wall paintings of the crypt of St. Stephan and the absence of this element in those referable to the upper church, suggested differences in the procurement of copper for the manufacture of EB. The presence of arsenic and lead in iron-bearing pigments detected in the wall paintings of the crypt and their negligible amount in those of the upper church, suggested that these pigments come from a different sourcing area.

In the church of St. Martin, the use of different pigments for the execution of the incarnate of the figures, the extraordinary state of conservation of minium, and the absence of green and blue pigments are remarkable features of the stucco decoration paintings.

Introduction

Only very few examples of Early Medieval wall paintings survive in Europe. Most of them have been discovered in the 19th and early 20th century. Since then, they have been in the focus of research into Early Medieval Art and Architecture. However, stylistic comparisons have yielded unreliable results, and the uncertain date of many paintings adds to the difficulty. In addition, Early Medieval wall paintings have not been always systematically studied and the available scientific data are fragmentary. The focus of the research project titled "Forgotten colors. Rediscovering the original polychromy of Early Medieval wall paintings in the *Raetia Curiensis* region" is a comprehensive and comparative study of Early Medieval wall paintings located in the Alpine territory that includes the current Swiss Canton of Grisons and parts of Northern Italy and Austria [1]. The aim of the research is to go beyond the iconography and materiality of the individual artistic objects (wall paintings and painted plaster and stucco fragments) and to tackle in-depth aspects that are often neglected in historical paint research. While the interdisciplinary study of wall paintings is well-established at the single site level, such a large comparative study, involving eight churches inside a larger but coherent region, is novel. This broad comparative approach will allow results

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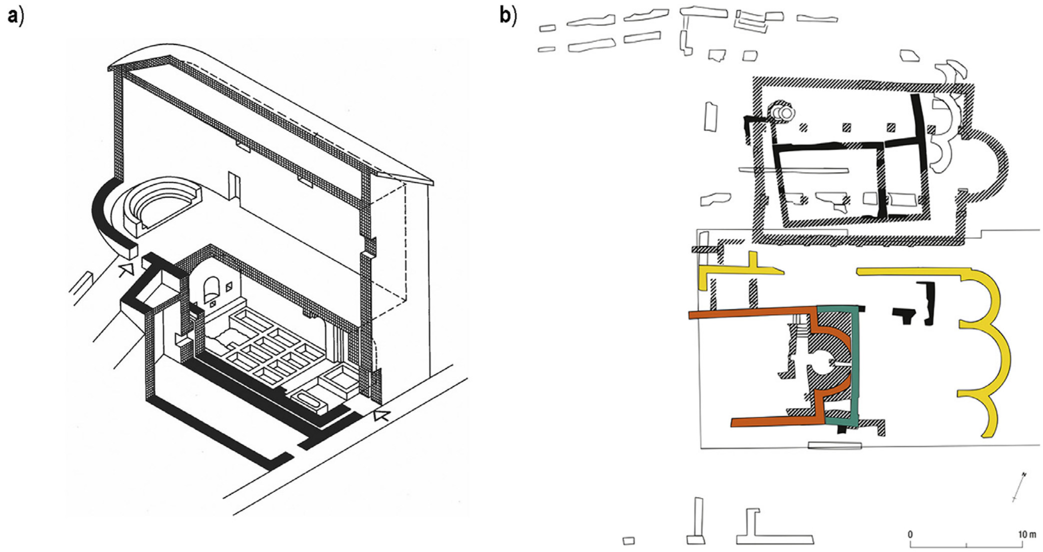

Fig. 1. a) Reconstruction of the St. Stephan's crypt and the church built on top of it in around 500 CE [19]. b) Excavation plan of the Disentis site by Hans Rudolf Sennhauser. Orange: first construction phase of the St. Martin's church around 700 CE (first construction phase). Green: rectangular choir added to the nave of the first construction in the middle of the 8th century (second construction phase). Yellow: Carolingian triple-apsed hall around 800 CE (third construction phase) [20].

which go beyond questions of materials, techniques and iconography by enabling us to trace the networks of people, materials and ideas involved in the creation of the painting cycles, and to track diachronic developments [2,3].

Several studies have been carried out on Early Medieval wall paintings located in Europe giving an important contribution to the knowledge of paint materials and techniques used. Research was carried out at St. Georg in Reichenau-Oberzell [4], St. Johann in Müstair [3,5-8], St. Maria *foris portas* at Castelseprio [9], St. Giulia in Brescia [10], St. Vincenzo al Volturno [11], St. Maria Antiqua in Rome [12,13], St. Saba in Rome [14], St. Clemente in Rome [15], St. Benedikt in Malles [3,7], and St. Peter upon Gratsch [16–18]. However, most of these studies are not comparable each other as the analytical techniques involved are not always the same, the aim of the research is different, and the design concept of the analytical campaign is variable. To overcome these aspects and to get comparable results at the scale of the individual sites (where different archaeological phases may occur) or between the sites (geographical scale), the basic same approach is used in the current project though specific research questions or features of a particular site may require different, complementary, integrative investigation methods.

This contribution presents the results of non-invasive surface and point analysis gathered in the crypt of the church of St. Stephan in Chur (wall paintings and painted plaster fragments; acronym SSC) and in the church of St. Martin in Disentis/Mustér (painted stucco fragments; acronym DIS) situated in Canton of Grisons.

The crypt of St. Stephan was erected in the 5th century; it is the largest surviving late-roman burial chamber in the North of the Alps. On its walls survive remnants of the pictorial decoration. The relics of the archmartyr Stephen, whose remains were discovered near Jerusalem in 415, were deposited in the crypt inside a niche in the wall. The crypt also functioned as burial place of the bishops of Chur. A church was built on top of the crypt around 500 CE (Fig. 1a). Like the crypt, it was richly decorated with mosaics and wall paintings. The building fell into ruin in the 16th century and was rediscovered in 1851. During the archaeological excavations carried out within the crypt in 1955-'57/1997-'99 and 2008, some wall paintings were preserved, and some detached and moved into storage [19]. A large number of painted plaster fragments was also recovered from the archaeological sediments. The wall paintings can be attributed to three main phases. Phases 1 and 2 are decorative phases within the crypt, while phase 3 is attested by painted mortar fragments which probably belong to the upper church. Another group (Phase 4) is attested by a few fragments with a special *cocciopesto* support found inside the crypt.

Excavations at Disentis Monastery, situated in a strategically important crossroads to the Lukmanier Pass, have yielded a remarkable number of painted stucco fragments from the 8th century. The fragments were discovered as early as 1908 and during comprehensive excavations in the years 1934 and 1980–1983. The latter was the most comprehensive archaeological endeavour under the guidance of Hans Rudolf Sennhauser. These findings played a crucial role in establishing a coherent chronological framework for the site and have provided a tangible link between the different construction phases, allowing the evolution of the site over the centuries to be clarified (Fig. 1b).

The first and oldest church of the monastery, a simple rectangular hall building (around 700 CE) is dedicated to St. Mary. Above this, in the first half of the 8th century, a three-nave hall with apse was built, later replaced around 800 CE by a three-apse hall, typical of the Early Medieval period in the Alpine area.

The first church of St. Martin (Fig. 1b, first construction phase) was probably erected in the first half of the 8th century. It was a rectangular hall church terminating towards the east with a horseshoe-shaped apse. Towards the middle of the 8th century, before 765 CE, a rectangular choir was added to the nave of the first construction (second construction phase). Large quantities of ornamental and figurative stucco reliefs and the remains of a floor mosaic made of soapstone cubes came from the rubble of the demolition of the second building of St. Martin and were used as levelling for the construction of the three-apse church. This detail provided a tangible link between the two phases of the building and allowed the archaeologists to attribute the stucco decoration to the second phase of the church of St. Martin.

Research aim

The main goal of the non-invasive campaign was to characterize the paint materials and to document the conservation state of the analysed surfaces. This work was very important for understanding

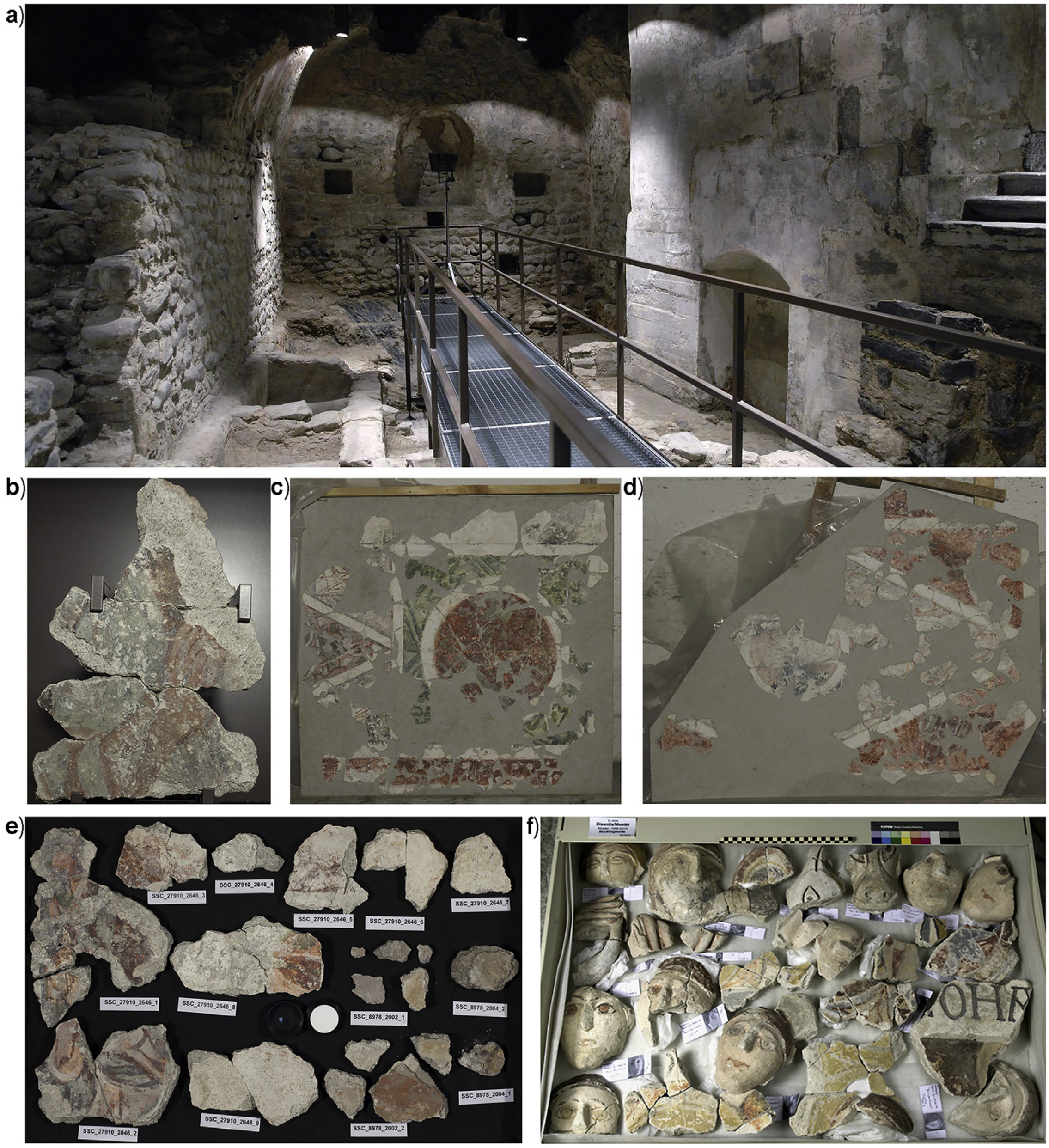

Fig. 2. a) Crypt of St. Stephan's church in Chur; b) painted plaster fragment preserved in the showcase inside the crypt; c-d) wall painting *stacchi*; e) a set of selected painted plaster fragments. f) Set of painted stucco fragments stored in the depot of the St. Martin's church in Disentis. (Photos ©SUPSI).

the execution technique of the wall paintings, and for making correlations between the painting materials and the different phases of the decorations. Finally, it laid the basis for the ongoing targeted and selective sampling strategy.

Material and methods

In-situ non-invasive investigations were carried out on the wall paintings and the painted plaster fragments from the church of St. Stephan in Chur (acronym SSC) and on the painted plaster stuccoes from the church of St. Martin in Disentis/Mustér (acronym DIS). Firstly, sets of images of selected painted surfaces were collected using technical photography in the visible (Vis), infrared (IR) and ultraviolet (UV) range. The images combined with a close visual examination of the painted surfaces guided the selection of the areas to be analysed with non-invasive spectroscopic techniques. The point analyses were carried out using Hand-Held X-Ray Fluorescence (HH-XRF), Fiber Optics Reflectance Spectroscopy (FORS) and reflection Fourier Transform Infrared spectroscopy (FTIR). The large volume of the collected point analyses is reported in the Supplementary Materials S1 (SSC) and S2 (DIS). This number was justified by the large areas of available painted surfaces, the variety of decorative motifs (faces, ornaments, inscriptions, dresses, vegetal and animal representations, imitation of marble, grounds), the different construction phases (SSC), and the variability of the chromatic tones and hues.

At SSC, the non-invasive investigations were carried out on the wall paintings in-situ (S1a), on a large recomposed painted plaster fragment preserved in a showcase inside the crypt (S1b), on two wall painting *stacchi* (S1c; detached wall painting sections), and on numerous painted plaster fragments (S1d; Figs. 2a-e). At DIS, the analyses were focused on selected painted stucco fragments (Fig. 2f, S2a) attributed to the 8th century decoration phase of the St. Martin's church (second construction phase).

Technical photography

Set of images were taken with a modified Canon 5D Mark II camera (built-in UV/IR block filter removed) equipped with an FF sensor (1.0x, format 36 × 24 mm^2) with a resolution of 21.1 megapixel. Each set consists of 7 types of photographic recordings (Vis, Rak, IRr, UVr, UVL, VIL and IRr_VIL) acquired by modifying radiation source and filters as necessary (Table 1S).

Hand-Held X-ray fluorescence (HH-XRF)

HH-XRF analyses were performed using the Niton™ XL3t 900 X-ray spectrometer by Thermo Scientific. The instrument is equipped with an X-ray tube (maximum voltage 50 kV), an Ag anode and a semiconductor Si-PIN detector which allows a resolution of 195 eV. Acquisition time was 60 s. This instrumental set-up is suitable for the detection of chemical elements with atomic number $Z \geq 16$ (i.e. from sulphur, S).

Fiber optics reflectance spectroscopy (FORS)

FORS analyses were performed with an AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source, both produced by Avantes. Detector and light source are connected with fiber optics to an FCR-7UV200–2–1,5 × 100 probe. The operational range was 375–1100 nm. Depending on the features of the monochromator (slit width 50 µm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra resolution is 2.4 nm calculated as FWHM. Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes. The investigated area is 1 mm in diameter. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1.0 s for each spectrum.

Reflection Fourier infrared spectroscopy (FTIR)

Non-invasive infrared analyses were carried out with the portable FTIR spectrometer ALPHA II by Bruker Optics. The instrument is equipped with a dedicated external reflectance module with specular optics (22°/22°) to collect the infrared radiation reflected from a surface at about 1 cm of distance. The system consists of a CenterGlow™ source, a RockSolid™ interferometer (with gold mirrors) and a temperature controlled DTGS detector. An integrated USB high-resolution video camera provides the view of the sampling area of ca. 3 mm diameter. The reflection FTIR spectra, expressed in pseudo-absorption units [A' = Log(1/R); R = reflectance], were collected in the spectral range of 8000–350 cm^{-1}, with a resolution of 4 cm^{-1} and using an average of 186 scans. Spectra from a flat gold mirror were used for the background correction.

Results and discussion

St. Stephan's church - Chur (SSC)

The support of the wall paintings of phases 1 and 2 differs markedly from that of phase 3. The paint layers in phases 1 and 2 are applied on a thin, white, polished, compact fine plaster, a few mm thick. The phase 3 intonaco has a coarser aggregate, grey colour, and is thicker. No definite observations could be made on the application mode of the paint, although the composition of the pigments (Table 1) may suggest both *a fresco* and *a secco* painting techniques.

Preliminary results about localization, distribution, and optical proprieties of the paint materials, emerged from the technical photography. Notably, some VIL records showed the typical infrared luminescence induced by visible radiation of the Egyptian Blue (EB) [21]. It was noticed on wall paintings (two areas on the East wall denoted by SSC_E_1 and SSC_E_2) and on archaeological fragments on areas ranging in colour from pale blue to violet and grey. The presence of EB was confirmed by combining the detection of copper (Cu) by HH-XRF with the FORS data (Figs. 3a-b and S1). Moreover, in some of the paint layers containing EB (first and second construction phases; S1), Cu was found along with zinc (Zn). The presence of Zn may be related to the use of a copper-zinc alloy (brass) as raw material [22] or to the metal ore sources [23]. At this stage, we can state that the raw material sources used for the manufacture of EB is similar for the first and second construction phases and different for the third one.

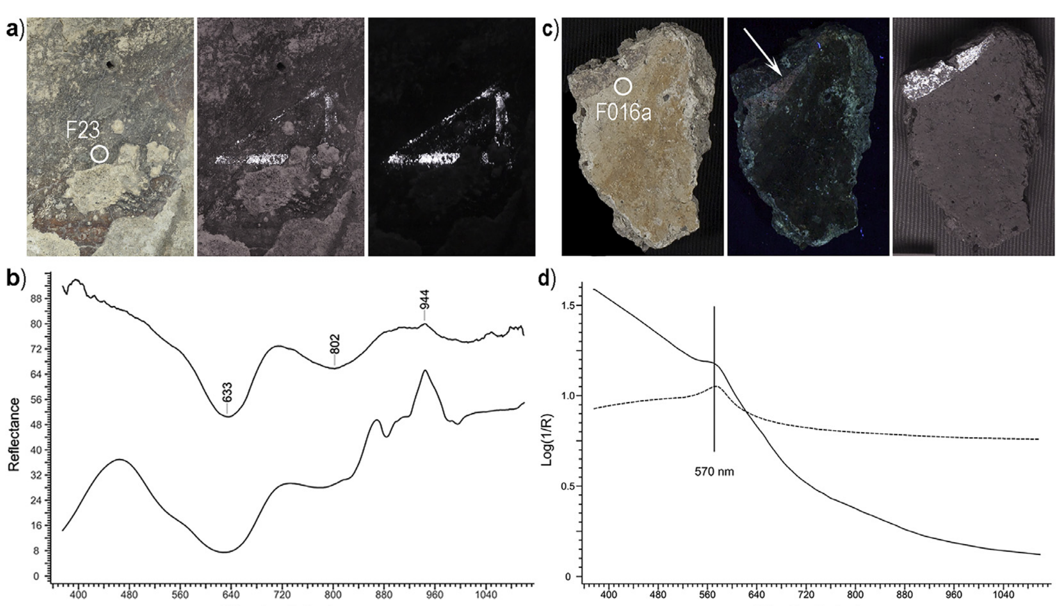

Fig. 3. a) Vis, IRr_VIL, and VIL records collected from the SSC_E1. b) FORS spectrum of the point F23 (top) compared with a reference spectrum of Egyptian blue (bottom). c) Vis, UVL and IRr_VIL records of the fragment SSC_8978_2002_1_e; d) FORS spectrum of the point F016a compared with the FORS spectrum collected in Müstair [7]. Both spectra are shown in pseudo-absorbance [A' = Log(1/R); R = reflectance].

Table 1
Summary of the pigments identified in St. Stephan's church in Chur (SSC).

St. Stephan's church in Chur (SSC)		
Archaeological phase	Colour	Pigments identified
I	green	green earth
I	dark green	
I	light green	
I	red	red ochre or iron-bearing pigment
I	light red	
I	orange	
I	light orange	
I	brown	
I	light brown	iron-bearing pigment
I	pink	
I	light yellow	yellow ochre or iron-bearing pigment
I	gray	mainly carbon-based pigment (?) mixed with different proportions of lime white
I	dark gray	
I	light gray	Egyptian blue mainly carbon-based pigment (?) mixed with lime white
I	white	mainly lime white and subordinately lead white
I	black	carbon-based pigment (?)
II	grayish blue/blue	Egyptian blue
II	green	green earth
II	red	red ochre or iron-bearing pigment
II	light red	iron-bearing pigment
II	orange	red ochre
II	brown	red ochre or iron-bearing pigment
II	light yellow	yellow ochre
II	gray	mainly carbon-based pigment (?) mixed with different proportions of lime white
II	dark gray	
II	black	carbon-based pigment (?)
III	red	red ochre or iron-bearing pigment
III	grayish red	Egyptian blue and organic dye (?)
III	orange	iron-bearing pigment red lead
		red and/or yellow ochre
III	light orange	red ochre or lead white
III	brown	iron-bearing pigment
III	light yellow	lead white or yellow ochre
III	gray	Egyptian blue lime white lead white
III	light gray	Egyptian blue or organic dye (?)
III	white	mainly lime white and subordinately lead white
IV	orange	yellow ochre and/or red ochre
IV	light yellow	yellow ochre

Table 2
Summary of the pigments identified for the site of St. Martin's church in Disentis (DIS).

St. Martin's church in Disentis (DIS)	
Colour	Pigments identified
red	red ochre or red lead
dark red	red ochre and/or red lead
orange	red lead lead white lime white red ochre
light orange	lead white and yellow ochre or red ochre
brown	red ochre yellow ochre lime white carbon-based pigment (?)
dark brown	red ochre yellow ochre red lead
light brown	red ochre or yellow ochre
Pink/light pink	red lead red ochre lime white lead white
yellow	yellow ochre
light yellow	
gray	mainly carbon-based pigment (?) mixed with different proportions of lime white
dark gray	
light gray	
black	carbon-based pigment (?)
white	mainly lime white

Interestingly, on three painted plaster fragments where EB was detected, very similar FORS spectra were obtained (points F008a, F016a and F018a) which coincide with that obtained from the convent church in Müstair [7]. One of these FORS spectra (point F016a) was collected from an area showing a pink UV luminescence (Fig. 3c) that could suggest the presence of an organic dye. However, this hypothesis needs to be verified by more specific analyses on sample like High Performance Liquid Chromatography – Mass Spectrometry (HPLC-MS) [24].

The UVL records of several painted plaster fragments showed an intense yellow UV luminescence corresponding to orange/light red and white areas. In these areas, high counts of lead (Pb) emerged by HH-XRF, while FORS and FTIR data allowed for the identification of red lead and lead white, respectively (S1). Specifically, the FTIR data revealed the presence of cerussite as primary mineral phase of the lead white, while hydrocerussite was clearly found only on a white/light grey area of a fragment (see points IR12/X190/F206 in S1-S1d). The UVL phenomenon observed could be related to the photo-luminescence properties of the lead white [25] and/or to an organic paint binder used for the application. However, only some infrared spectra collected from the fragments showed weak signals ascribable to oxalates, probably calcium oxalates, maybe produced by degraded organic material [26]. Red lead, lead white and the possible organic dye were found exclusively on fragments attributed to the third construction phase of the building.

The combination of HH-XRF and FORS data provided the characterization of pigments like green earth, red and yellow ochre. On some green areas, copper (Cu) and/or arsenic (As) were identified through HH-XRF, in addition to the green earth detected by FORS. Arsenic was also detected on certain dark red areas. The identification of As could be relevant for provenance studies of the raw materials [27] and this topic will be further investigated by planned micro-invasive analyses. The presence of As (and Pb) has been confirmed only in the first and second decoration phases of the crypt, whilst these two elements are negligible for the third one.

Most of the black/grey areas examined were probably executed with a carbon-based black pigment. In addition, some of these areas, belonging to phase 3, showed high counts of lead. Since in this phase both red lead and lead white have been identified, the grey paints could either consist of a mixture of lead white and a black pigment, or of degradation compounds of the lead-based pigments. The gray tones corresponding to the use of EB can be correlated with discoloration processes affecting the pigment most probably due to superficial deposition [28].

Overall, most of the FTIR spectra collected from SSC showed the common presence of calcium carbonate coming from the plaster and sulfate and/or silicate components that could be related to pigment formulations [29] or surface deposits. The different hues of the painted surfaces executed with the same tipology of pigment (Table 1) may be the consequence of different binder/pigment ratios or admixture with lighter pigment.

St. Martin's church – Disentis (DIS)

The stuccoes of Disentis consists of a fine, white lime mortar. The paint layers were applied on a layer of white limewash. Painting plays a predominant role within the sculptures, not solely to accentuate sculptural details, but rather to amplify the impact of the paintings themselves.

Technical photography records of the painted stuccoes provided information especially on the presence and distribution of painting areas with UV luminescence phenomena. These areas were analysed by FTIR to verify the possible presence of organic material, but only lead white, primarily cerussite, was recognized in correspondence of pink, orange, and grey areas with yellow-orange UV luminescence (Figs. 4a-d). In addition to lead white, on the pink and orange areas FORS analysis revealed the presence of red lead (Fig. 4e). This pigment, mixed or not with other pigments, was extensively used for the paint decorations (S2). Since lead white was never found on white areas, but always in conjunction with red lead, it is as yet unclear if was used mixed with red lead, or if it is present as an impurity.

On yellow and red/brown iron-rich areas, FORS allowed for the identification of yellow and red ochre, respectively. However, in several HH-XRF spectra of these areas lead was also detected. It is probably related to lead-based pigments mixed with ochre or applied on the underlying paint layer. Black and grey tones were most likely obtained with a carbon-based black pigment. Surprisingly, no blue or green pigments were used for the painting decoration of the Disentis stuccoes.

Two types of pink-coloured incarnate could be differentiated, with and without lead. In these areas, FORS detected red lead and red ochre, respectively.

The good preservation of the red lead, which is prone to deterioration in alkaline conditions such as those existing on wet lime plaster [30], suggests that the paint layer was very likely applied *a secco*. However, very little evidence has been found for organic binders. Indeed, the presence of an organic material (C=O and C-H bands detected by FTIR) can be supposed only on a single fragment with a red lead layer (point IR33, S2). In addition, some IR spectra showed a weak band at ca. 1320 cm^{-1} ascribable to possible oxalates [26]. As reported for SSC, different ranges of hues obtained using the same pigment were detected in DIS (Table 2).

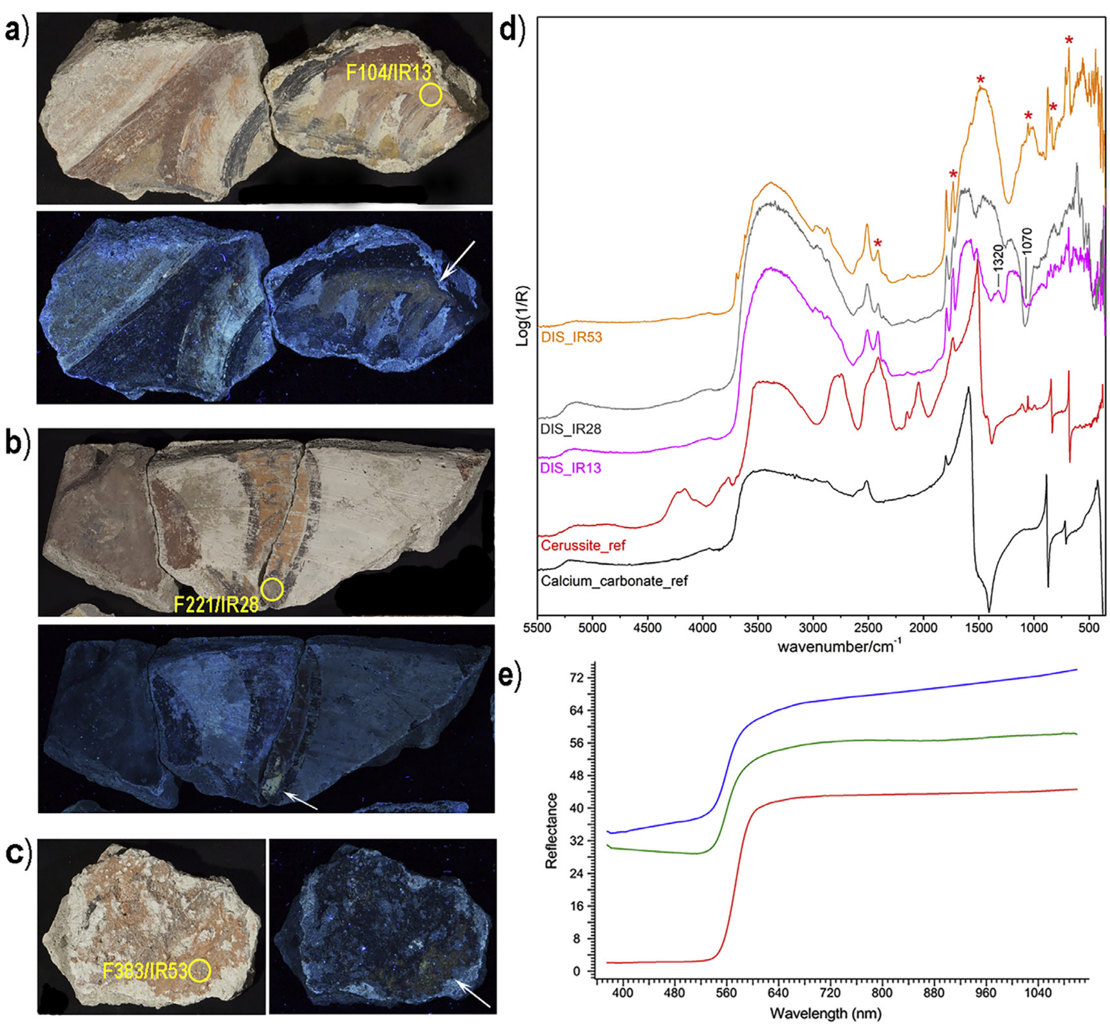

Fig. 4. Vis and UVL records of the fragments: a) DIS_04_15, b) DIS_18_43, c) DIS_48_98 d) Reflection FTIR spectra of the points IR13, IR28, and IR53 compared with reference spectra of calcium carbonate (black profile) and cerussite (red profile). Cerussite bands are marked with a red asterisk. The bands at ca. 1320 and 1070 cm^{-1} could be correlated to oxalates and a silicate component, respectively. e) FORS spectra of the points F104 (blue profile), F383 (green profile) compared with a reference spectrum of red lead (red profile).

Conclusions

The non-invasive analyses conducted at the churches of St. Stephan in Chur and St. Martin in Disentis/Mustér represent an initial step in the systematic comparative study of Early Medieval wall paintings in the *Raetia Curiensis* region.

The 5th century wall paintings of the crypt of St. Stephan align with the antique tradition and generally do not feature lead-based pigments [31]. A clear distinction in the colour palette is observable between the paintings on the East wall and those on the other walls, as EB was only detected on the East wall. The question remains whether this distinction indicates a chronological gap between the paintings or is influenced by iconography. Additionally, significant differences have been observed between the painted plaster fragments attributed to the crypt and those linked to the upper church. The plaster and pigment composition of the upper church display similarities with later wall paintings, such as those in St. John in Müstair (8th century) [7]. This primarily concerns the use of lead-based pigments and possibly an organic dye associated with EB. The latter seems to have different copper sources as only the painted surfaces from the crypt contain Zn. This additional difference is significant since the construction date of the upper church is not well dated. While the crypt paintings appear to be still firmly rooted in Antique tradition, the upper church aligns more with Early Medieval sites. The presence of chemical elements in the paint layers of the crypt like As in red and green areas, and Zn with EB, points the way for further studies and interpretations regarding the technology of pigment production and provenance.

Notably, for St. Martin church in Disentis the palette differs considerably from other Early Medieval sites, as it lacks greens and blues. The remarkable preservation of paint layers with red lead is another unique aspect, with no prior instances of such stability encountered in wall paintings from this epoch. The cause behind this exceptional durability of the red lead pigment will be a central focus of further research. The investigations allowed for the identification of two different types of incarnates, one containing a lead-based pigment, the other not. This indicates that within the stucco decoration, there were areas or scenes executed with different pigments. The application of the paint layers on top of a limewash as well as the stucco execution of the intonaco clearly set this cycle apart from the other ones studied in the present project. Some aspects such as the painting on a limewash layer point to the Byzantine world [32]. However, this is also attested in the Anglo-Saxon area. The integration of painting and sculpture can be found in Anglo-Saxon as well as in Lombard churches [33,34]. The non-invasive analysis of the Disentis painted stuccoes confirmed their very distinctive nature, which until now finds no parallels in Europe.

The results presented in this paper have provided the foundation for several new hypotheses and questions, which will be examined using micro-invasive methods in the subsequent stages of the project “Forgotten Colors”.

Acknowledgements

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2024.03.019.

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