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ORIGINAL PAPER

Preliminary non-invasive study of Carolingian pigments in the churches of St. John at Müstair and St. Benedict at Malles

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Abstract

The monastery church of Müstair (Val Müstair, Switzerland) and the church of St. Benedict in Malles (Obervinschgau, Italy) contain painting cycles dating to the late eighth/early ninth century which are considered among the best preserved in Europe. Located inside a region of strategic importance at least since Roman times, during the medieval era both areas formed part of the diocese of Chur and were politically and culturally closely linked; the present border, in fact, developed in the course of the early modern period.

The two painting cycles have been studied with a non-invasive approach using spectral multiband imaging, UV-visible diffuse reflectance spectrophotometry with fiber optics (FORS) and X-ray fluorescence spectrometry (XRF). The combined application of these techniques gave important insights into the painting techniques used in the two cycles. Clear similarities in the palette of pigments appeared; the colour palette included mainly materials typically used in medieval mural paintings, such as red and yellow ochres, carbon black, *Bianco di San Giovanni* and green earth, but lead pigments, such as red lead and massicot, which are less suited for use on plaster surfaces, were used as well. Of particular interest is the use of Egyptian blue and ultramarine blue that makes these paintings among the first in which the precious lapis lazuli pigment had been used in Europe. The occurrence of Egyptian blue and ultramarine blue puts the paintings closer to the ancient Roman than to the Romanesque tradition. A surprising result was the identification of As, which might indicate the use of orpiment for the creation of the wall paintings.

Keywords Pigments · Mural paintings · Spectral multiband imaging · FORS · XRF · Carolingian · Lombard

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Introduction

Historical framework: the political and geographical situation of Alta Val Venosta

The monastery complex of St. John in Müstair[1] and the church of St. Benedict in Mals/Malles[2,3] are outstanding examples of the art and architecture of the late eighth and early ninth century. They are located in the Eastern Alps, in the valleys of Müstair and Obervinschgau/Alta Val Venosta,[4] a region which is known for its many early medieval and Romanesque churches. Although they lie only about 15 km apart, today the two churches belong to different countries, Switzerland and Italy. The present border developed in the course of the early modern period. During the medieval era, both the Val Müstair and the Val Venosta formed part of the diocese of Chur and were politically and culturally closely linked.

The region was of strategic importance at least since Roman times because of its mountain passes, which allow a safe crossing of the main alpine divide (Fig. S1). The *Via Claudia Augusta*, built by the Romans after the conquest of *Raetia* in the late first century BC, followed the Val Venosta and remained one of the most important north-south routes through the Alps well into the early modern period (Grabherr 2006). From the sixth century onward, the area came under the influence of the Merovingian and Frankish rulers, who had to contend with the neighbouring Lombards to the south and Bavarians to the east. In the late eighth and early ninth century, the whole area was part of the territory of *Raetia Curiensis*, ruled on behalf of the Frankish king by the bishop of Chur, who until 806 exerted temporal as well as religious power. After the incorporation of the diocese into the Frankish kingdom, in the early ninth century, Charlemagne reorganized its administrative structure by separating the religious and secular powers (Goll 2013).

The construction date of the monastery church of St. John in Müstair (Fig. S2) can be precisely set by dendrochronology. A wooden beam preserved in the eastern gable was felled in the winter of 775/776 AD (Hurni et al. 2007). In the medieval period, timber for the construction of buildings was usually felled in winter and processed in the following months (Descoeudres 2007). This means that the construction of the church was completed in or after the year 776.

The construction of the church of St. Benedict in Malles (Fig. S3) cannot be dated so precisely. The frescoes on its inner walls have been attributed stylistically to the early ninth century (Emmenegger and Stampfer 1990; Rasmo 1981). Emmenegger and Stampfer (1990) observed the presence of two layers of limewash underneath the painted decorations. Since the top layer had a yellowish tinge, they deduced that it had been exposed to the environment for a longer period of time during which the interior had remained without painted decoration. Based on this observation, Nothdurfter (2003) proposed a construction date of the church in the mid-eighth century. However, the presence of yellowish limewash layers is not a reliable chronological indicator. The significance of the yellowish tinge would need to be confirmed experimentally, while the presence of layers of limewash only shows that the surfaces have been whitewashed prior to the creation of the wall paintings and that this limewash has had time to a complete carbonation, which would not take more than a few months. Therefore, the question of the detailed chronology cannot be answered without further, more detailed analysis of the materials. The church itself is mentioned for the first time in a document from the twelfth century, which records the transfer of ownership from the bishop of Chur to the monastery of St. John in Müstair.

Because of its monumental size and strategic location, the construction of the large monastic complex of Müstair has to be attributed to the initiative of the bishop of Chur, the Frankish court or both. The court had great interest in securing its control of the territory and the important roads leading through the alpine passes (Goll 2013). In 881, the monastery was ceded by the Emperor Charles III, known as Charles the Fat, to the bishop of Chur (Müller 1981). The size of the first Carolingian monastery, as known from archaeological excavations, is comparable to other important monasteries of the time, such as the monastery of Reichenau (Lake Constance, SW-Germany: Zettler 1988) or San Vincenzo al Volturno (Molise, Central Italy: Hodges 1993). It possessed two sacred buildings, the monastery church, a three-apse aisleless church with two annexes to the north and south, each with its own apse and connected to the nave by large arches, and the detached Holy Cross Chapel, to the south, with a trefoil-shaped layout, an upper floor and a lower floor used as crypt (Fig. S4A and B). The monastery church and the Holy Cross Chapel were decorated with frescoes and choir screens of sculpted marble. The Holy Cross Chapel was also provided with rich stuccoed decoration.

The church of St. Benedict at Malles is a small rectangular building (9.4 × 5.5 m, h 5.2 m) (Fig. S5). Its eastern wall is structured by three arched niches. The church was originally richly decorated with wall paintings. Today only those on the eastern wall and, partially, on the northern wall remain. Those on the southern and western wall are lost. The church can be linked to the upper hierarchies of the Frankish kingdom thanks to two extraordinary representations of a Frankish nobleman and cleric on the eastern wall of the church, known as "the benefactors". Different interpretations exist as to the identity of the individuals depicted. The layman could be a royal

[1] 46°37′47.460″N 10°26′56.340″E (WGS 84 lat/lon). Source: Bundesamt für Landestopografie swisstopo (map.geo.admin.ch).

[2] 46°41′25.150″N 10°32′22.280″E (WGS 84 lat/lon). Source: Autonomous Province of Bolzano/Bozen (gis2.provinz.bz.it).

[3] "Malles" thereafter

[4] "Val Venosta" thereafter

official, perhaps a count, while the cleric is thought to be a bishop or an abbot. It is clear from the prominent position of the portraits and the fact that the cleric offers a model of the church to the figure of Christ in the central niche that they played an important role in the construction of the church (Emmenegger and Stampfer 1990; Le Jan 1995, 113). The high status of the building is further emphasized by the presence of rich painted and sculpted decoration. The quality of the paintings in St. Benedict, especially those on the eastern wall, can be compared to the frescoes in Müstair. In both churches, the interior was subdivided by sculpted marble screens. The rich stucco decorations of St. Benedict finds a parallel in the Holy Cross chapel at Müstair (Feldtkeller and Warger 2017).

Because of the clear parallels between the churches of Müstair and Malles, their historical, archaeological and scientific study is best carried out if both sites are addressed in a comparative manner.

The painting cycles: presentation of the cycles, past art-historical research, painting techniques and importance

The monastery church of St. John in Müstair contains the only cycle of wall paintings of the eighth century with an iconographic program that can be reconstructed in its entirety (Sforza Vattovani 1976) (Fig. S6). The interior wall surfaces of the church and the two annexes were completely covered in paintings. Based on stylistic and iconographic observations, Matthias Exner et al. (Exner 2004) have suggested that the paintings might date to the second quarter of the ninth century. The current restoration work, however, has shown that an underlying layer of limewash was still white and free from any dirt and soot when the plaster for the wall paintings was applied. Based on this observation, we are of the opinion that the painted decoration was added not long after completion of the church in the last quarter of the eighth century. The "late" dating of the paintings on the basis of iconographic criteria has recently been criticized by Sennhauser (2019). Those in the annexes are now largely lost. The paintings in the church on the other hand are largely preserved and convey a sacred narrative which surrounds the observer. Scenes from the life of David in the upper registers are followed from top to bottom, in chronological order, by scenes from the life of Christ and the Apostles. On the eastern wall of the nave, above the three apses, the Ascension of Christ forms the prelude to his triumphal return in the End of Time depicted on the western wall of the church. The celebration of Christ finds its conclusion in the semi-domes of the three apses with his depiction as universal judge, conqueror of death and founder of the Christian Roman Church. In the scenes below the semi-domes, the paintings narrate the life and martyrdom of St. Peter and Paul (northern apse), St. John (central apse) and St. Stephen (southern apse). Sometime after their damage by fire, probably in the eleventh century, the wall paintings were covered by a layer of limewash. A layer of Romanesque frescoed paintings, dated stylistically to the late twelfth or early thirteenth century, was added on the eastern wall and inside the three apses and probably also in the annexes of the church. To increase the adhesion of the new layer of plaster, numerous little holes were picked into the original wall surface, severely damaging the Carolingian frescoes. In subsequent periods, further layers of plaster, painting and limewash were added to the church, covering the Carolingian and Romanesque paintings completely (Wyss et al. 2002; Goll et al. 2007).

The frescoes were rediscovered in 1894 by the art historians Josef Zemp and Robert Durrer. At that time, only the paintings under the roof of the church, above the gothic vaults of the late fifteenth century, were visible (Zemp and Durrer 1906-1910). In 1908, these were removed with the *strappo* technique and brought to the Swiss National Museum in Zürich. The remaining frescoes inside the nave and the apses of the church below the gothic vault remained covered by later layers of plaster and paint until they were brought to light and heavily restored between 1947 and 1951. Their appearance today is influenced not only by environmental factors, which include at least two fires in the church, but also by this heavy-handed restoration work (Wyss 2002). As a consequence, the original polychromies of the paintings are reduced today to brown, red and grey tones. Also, the upper paint layers are mostly missing. The resulting appearance has been further accentuated by the retouches of the 1940s and 1950s. Art-historical studies in the past have not taken this situation into account and therefore do not give a correct assessment of the style and technique of the frescoes. Only in the course of recent analytic and restoration work from the 1980s onward, mainly by Oskar Emmenegger (2002), has it been possible to understand these factors better. Because of this, most art-historical studies of the paintings at Müstair prior to this date are severely limited in their reliability (Wyss et al. 2002).

Early art-historical analyses, which were based on the unrestored frescoes from the attic of the church, saw a similarity in style and technique between the paintings in Müstair and Malles (Garber 1915). Nicolò Rasmo (1966), whose view of the frescoes was determined by the already restored paintings, saw things differently. He considered the frescoes in Müstair to be of lesser quality and later date than those in Malles. Fulvia Sforza Vattovani (1976) assumed that the wall paintings in Müstair were conceived as monochromatic images. With the aforementioned reappraisal and detailed study of the painting technique carried out by Oskar Emmenegger (2002), supported by scientific analysis of the pigments and mortars, a new basis for the study and the interpretation of the paintings in Müstair has been laid. Not only the stylistic but also the technical and material aspects of the paintings will have to be reappraised and compared with other work of this period, in particular with the paintings in St. Benedict in Malles.

In the church of St. Benedict, two styles of painting can be identified. One is found inside the niches and in the angel frieze on the eastern wall and the other between the niches on the eastern wall (depictions of the benefactors) and on the northern wall. On the eastern wall, the main scenes are located inside the three niches, originally framed by columns and arches made of stucco. They depict Christ surrounded by angels in the central niche, Saint Gregory in the northern niche and St. Stephen in the southern niche. In the spaces between the niches, two figures have been depicted: a man dressed like a Frankish noble and another person with a tonsure dressed in cleric's garments. The head of each figure seems to be surrounded by a square nimbus. These realistic figures are commonly referred to as the founders, or benefactors, of the church. The nobleman holds his sword in front of him as if to stress his role as count or sword-bearer; the cleric presents a model of the church to teh figure of Christ in the central niche. The chronological sequence proposed by Emmenegger and Stampfer (1990), which supposes a longer hiatus between the construction of the church and the creation of the painted decoration, contrasts with the definition of the two persons as founders of the church, which is why we prefer the term benefactors. Above the niches, a frieze with angels completed the eastern painting cycle and seems to follow the classic patterns typical for apsidal decorations (Fig. S7). The chronological sequence among these different paintings cannot be determined, since there is no stratigraphic connection among them.

On the northern wall, two horizontal bands of paintings are preserved. Their interpretation is made difficult by their fragmentary condition. In the upper register, one scene in the east has been associated with the life of St. Gregory. The scenes towards the west are commonly identified as relating to the life of St. Paul (or King David, according to others), while in the lower register, the life of St. Benedict may be depicted (Rasmo 1981) (Fig. S8).

The dating of the painted decoration of the church of St. Benedict in Malles is based on stylistic and historical criteria. The commonly accepted interpretation dates the paintings to the late eight/early ninth century. The attribution of the paintings to particular workshops has been widely discussed. While the paintings in the niches and, probably, the angel frieze on the eastern wall can be attributed to a different workshop than those on the northern wall and those of the benefactors, between the latter two groups there are differences as well as common elements. The differences could be the result of different artistic traditions coexisting within a single workshop, as most critics have proposed (Garber 1915; Emmenegger and Stampfer 1990; Rasmo 1981), or they could indicate different phases in the decoration of the church. As in Müstair, in Malles, the surfaces of the frescoes have been reduced and modified by the passing of time, which makes stylistic interpretation difficult.

The wall paintings in the church of St. Benedict in Malles have not been subjected to the same amount of scrutiny as those in Müstair. However, their importance was recognized very soon after their complete uncovering in 1913. The representations of the two benefactors of the church on the eastern wall have been reckoned among the best examples of Carolingian painting (Sforza Vattovani 1976). A detailed study of the painting technique has been carried out by Oskar Emmenegger; Helmut Stampfer has attempted an art-historical reappraisal of the frescoes, based on Emmenegger's findings (Emmenegger and Stampfer 1990). Like Garber (1915) before them, they considered the frescoes on the eastern wall of St. Benedict to be closely related to the frescoes in the monastery church of Müstair.

In this context, a detailed analysis of the technical and material characteristics of the various representations may help to understand better the development of the pictorial sequence in St. Benedict and provide further elements of comparison with the monastery church of Müstair and other schemes of painting cycles of the eighth and ninth centuries.

Considerations of past restoration works

The discovery and the subsequent treatment of the remnants of Carolingian frescoes in the attic of the convent church of Müstair by Josef Zemp and Robert Durrer in 1894 had important repercussions for their conservation. The frescoes were removed with the *strappo* technique in 1908 and 1909 and brought to the Swiss National Museum in Zürich, suffering severe damage in the process. Inside the church, part of the Romanesque painting behind the baroque side-altars in the northern and southern apse was brought to light (Zemp and Durrer 1906-1910). After these deleterious interventions at the turn of the twentieth century, the frescoes in the church were left untouched until a complete restoration begun in 1947. In only 4 years, the restorer Franz Xaver Sauter removed all the plaster and the paint layers later than the Carolingian and Romanesque frescoes, which were thus brought to light. Sauter used a mortar with a high gypsum content to close holes and fissures. In those areas where he was not able to remove layers of limewash from the surface of the frescoes, he resorted to applying a thin coating of plaster, on which the underlying scene was repainted. Sauter also used fixatives and applied a coating of tempera to increase the contrast and brilliancy of the paintings. In 1951, after the completion of the restoration, almost all traces of painted decorations earlier than the Romanesque period had been erased. The heavy-handed reconstruction altered the perceived style of the paintings considerably.

Regular monitoring of the paintings carried out since 1967 showed that the restoration had other long-term deleterious effects on the wall surfaces due to the action of salts, fungi and algae. After several measures taken in the 1980s, such as the removal of the heating system, the cleaning of the surfaces of the frescoes and the construction of a better drainage system to keep moisture from the church walls, the condition of the frescoes stabilized (Emmenegger 2002). The observed deteriorations, in particular the deposition of dirt which formed a substrate for the growth of fungi, were concentrated on those areas which had been heavily restored between 1947 and 1951. Furthermore, cracks and voids underneath the Carolingian and Romanesque plaster were a cause of concern. In order to guarantee the preservation of the frescoes for the future, it was decided, after a lengthy decision-making process involving a group of international experts (Wyss 2002), to remove the additions of the 1940s and 1950s wherever they lay directly on painted surfaces and to subject the frescoes to a careful conservation treatment. The new restoration of the painted surfaces at Müstair began in 2012 and is still ongoing. By removing the layers of paint and plaster covering the frescoes, new insights are being generated on the style and painting technique. The uncovering of the Carolingian and Romanesque surfaces and paint layers also offers the possibility of carrying out analytical work on the mortars, pigments and binders used by the medieval artists.

Restoration work on the wall paintings of the church of St. Benedict in Malles began at the end of the nineteenth century. In 1914, after the uncovering, securing and cleaning of the depictions of the so-called benefactors and of the upper areas of the paintings on the northern wall (Rüber 1991), the walled-up niches in the eastern wall were opened. The paintings inside the niches, covered by limewash, were brought to light together with the so-called angel frieze at the top of the eastern wall. Fragments of the stucco decoration of the eastern wall were recovered from the fill inside the niches,[5] and a stucco pillar was discovered behind the northern retaining wall (Nothdurfter 2002). Because of the precarious situation of the painted plaster of the figures of the benefactors, their removal was briefly considered, before deciding that the dehumidification of the walls was a more sensible solution to the problem. The following excavation work which took place in the church led to the recovery of 1923 fragments of plaster with ornamental painting[6] and of a number of stucco fragments. In the following year, further conservational measures were applied to the wall paintings. The heritage conservation department, wishing to conserve the paintings while also protecting their authenticity, tasked the painter Tullio Brizi with the conservation work, instructing him to stabilize the surfaces without any in-painting.

In the course of renovation work on the roof and walls in the years 1954–1956, the northern retaining wall, which until then had covered the lower two thirds of the painted wall surface, was removed. This was done without due care and without a proper study of the surviving paintings, so that the procedure incurred severe criticism (Rasmo 1966, 1981). Furthermore, the remaining plaster and limewash covering the paintings on the eastern wall were removed. Underneath, the preparatory drawings and the holes left by the pegs anchoring the stucco decoration came to light the stucco decoration came to light. The present condition of the wall surfaces goes back to interventions in the years 1962/1963, when further parts of the paintings were exposed, cleaned and stabilized. The cement plaster applied in previous interventions was removed. By lifting the ceiling to its original height, the topmost border of the frescoes became visible again. In 1995, preventive maintenance measures were carried out. Besides the removal of dust and the closing of single large cracks, the stabilization of detaching areas of plaster inside the depiction of the benefactors was the most important and urgent intervention (Mayer 1995).

The main causes of damage – the improper use of the building before and during the two World Wars, the partially unprofessional treatment of the frescoes, as well as the repeated strain posed by humidity – have been removed thanks to three dehumidification interventions, the careful measures taken by the present ownership and to considerate use of the church. The problem of the detaching of the painted plaster from the wall was still observed during a survey and mapping of the condition of the paintings carried out in 2015 and is unlikely to be solved easily. The detachments pose a threat to the paintings only in localized areas and have been stabilized in the course of maintenance interventions in a minimalist way. How these areas will behave in future has to be ascertained by periodic monitoring with the help of the available damage maps.

Previous scientific research on pigments from the eighth/ninth century

Scientific research on pigments used in the execution of Carolingian era wall paintings in the Raetian context is rather limited. Only in the monastery church of St. John in Müstair have the paint layers been subjected to systematic analysis. The first scientific analysis was carried out in 1975 by Hermann Kühn, followed in the 1980s by Franz Mairinger. The results of these studies are documented in detailed reports, which are deposited in Müstair in the archive of the Foundation Pro Monastery of St. John, and have been published by Mairinger and Schreiner (1986) and by the conservator and restorer Oskar Emmenegger in his papers on the painting technique of the frescoes (1998).

The following pigments were identified by Kühn and Mairinger in the Carolingian paint layers in the church of St. John: *Bianco San Giovanni* (lime white), altered Pb-based

[5] Currently stored by the Municipality of Malles
[6] Currently stored by the Municipality of Malles

pigments, red and yellow Fe-rich pigments, massicot, sometimes mixed with yellow ochre (Mairinger suggests the massicot could be a deterioration product of lead white), carbon black, a red lake and Egyptian blue (Mairinger and Schreiner 1986). While, according to the report of the analyses compiled by Mairinger, two samples were found to contain ultramarine blue, this observation is not mentioned in his published articles. Emmenegger, on the other hand, describes the use of blue pigments as follows: “For shadow tones, the painter also used a mixture of Egyptian blue, ochre and lime (applied *al fresco*). There are also Egyptian blue coloured grounds, and in rare cases halos with a calcareous underpainting with a light lapis lazuli overlay” (Knoepfli and Emmenegger 1990).

The pigments used in the execution of the wall paintings in St. Benedict in Malles were never analysed using scientific methods. According to Emmenegger and Stampfer (1990), a red dye was identified on some fragments recovered in 1923. However, no written report of the analysis seems to have survived.

The present study

In 2017 and 2018, initial analyses by spectral multiband imaging have been carried out in the Monastery Church of St. John at Müstair and in St. Benedict in Malles. Based on the results, a non-invasive interdisciplinary diagnostic campaign was designed in order to understand better the nature and the chemical composition of the pigments used for the Carolingian paintings, the relationship between the two sites and possible alteration processes. In situ investigation methods were used: Spectral multiband imaging, UV-visible diffuse reflectance spectrophotometry with fibre optics (FORS) and handheld X-ray fluorescence spectrometry (HH-XRF).

Materials and methods

Brief description of current documentation methods

The ongoing restoration of the wall paintings in the monastery church of Müstair is accompanied by a detailed photographic documentation depicting the situation before, during and after the intervention, carried out by members of the restoration team. High-definition digital photographs taken with a medium-format camera allow for the documentation of details in the submillimetre level. Typically, panoramic photographs as well as macros of details deemed important by the restorers are taken. These include photographs in raking light which allow the documentation of the morphology of the surface as well as the stratigraphy of the paint layers. These visible light photographs are complemented by uncalibrated photographs in UV light, which use a UV filter in combination with a yellow filter in front of the camera in order to capture the UV fluorescence of the surface.

Both the UV fluorescence and the visible light photographs are designed to document the restoration work, and also serve as an analytical tool in their own right, as at large magnifications and with raking or UV light observations relating to painting techniques and paint layers can be made which would not be possible with the naked eye. Based on these observations, questions are formulated which are then investigated with analytical methods carried out by specialized professionals.

Spectral multiband imaging

In addition to the photographs taken by the restorers during the restoration campaign, professional spectral multiband imaging (SMI) was carried out in selected areas. Spectral multiband imaging is a non-invasive application of imaging, used for studies of materials and painting techniques, which generates a set of images in different spectra (visible, raking light, UV reflectance, UV false colour, UV Fluorescence, IR Reflectance, IR False Colour, IR Fluorescence Vis-induced), following standards described in 2013 by Dyer et al. (2013). It shows abnormalities, similarities and differences on the surface, based on the physical and chemical properties of materials, which determine the degree of reflection, transmission and absorption, thus generating information of various kinds. Thanks to this method, areas to be clarified with other examination methods can be determined with pinpoint accuracy. With the latest generation of CMOS sensors and LED light sources, it has become possible to record digital images with improved quality in terms of spatial resolution of up to 151 MP and with improved signal-to-noise ratio and spectral resolution. Optical properties of different substrates and especially pigments that are relevant for spectral multiband imaging include specular and diffuse reflection, transmission, absorption and luminescence. Similar pigments under visible light may have different reflection spectra in the UV and IR range of electromagnetic spectrum that can be imaged by CMOS detectors.

Knowledge of the reflection and transmission behaviour of filters and lenses, of the spectral sensitivity of the camera sensor and of the emission spectrum of the illumination sources plays a central role in the calibration of spectral multiband imaging. Reflectance and luminescence targets have been used for standardized processing, image verification, reproducibility and repeatability. Calibration of diffuse reflection and luminescence was carried out with optical PTFE (2–99% reflection in the range of 200–2500 nm). The 100% reflection target used a polished specular sphere that covers the full range of camera sensitivity (320–1150 nm). In all reflectance recordings, the position of the lamps and also of unwanted stray light was documented. For the almost 100% absorption, a light trap has been used. The resulting set of images in different wavelength ranges (350–1150 nm) was calibrated and edited and then evaluated and compared to reference materials. For this purpose, well-known and prepared reference pigments and materials have been used. They have been prepared with different binders (egg and oil) and in pure form as powder. Three different sources of reference materials were available and have been used for the evaluation (Staatliche Akademie der Bildenden Künste Stuttgart, CHSOS, Opificio delle Pietre Dure Florence – Caruso 2009). The camera used had the following specifications: full frame medium format CMOS RGB sensor, modified to detect the whole range of sensor sensitivity, with a resolution of 101 MP, 11608 × 8708 active pixels and output image dim 300 dpi of 98.3 cm × 73.2 cm Table 1.

In situ FORS

FORS is widely used as a preliminary technique in order to have a fast, easy-to-obtain survey of the colourants on a painted artwork (Picollo et al. 2018). Due to the availability of portable systems, FORS measurements can be carried out in all instances and in particular in troublesome situations such as when analysis is to be carried out on scaffoldings.

FORS analysis was performed with an Avantes (Apeldoorn, the Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source; detector and light source were connected with fibre optic cables to an FCR-7UV200-2-1,5 × 100 probe. In this configuration, both the incident and detecting angles were 45 ° from the surface normal, in order not to include specular reflectance. The spectral range of the detector was 200–1160 nm; the overall operational range of the device (combination of lamp + detector) 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 was 2.4 nm calculated as FWHM. Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at 98% or more in the spectral range investigated. The investigated area on the sample had a 1-mm diameter. The probe was inserted into a block, in order to exclude external light and to hold the probe firmly in place. In all measurements, the distance between probe and sample was kept constant at 2 mm. To visualize the investigated area on the sample, the block contained a USB endoscope. The instrumental parameters were as follows: 10-ms integration time, 100 scans for a total acquisition time of 1.0 s for each spectrum. The whole system was managed by means of AvaSoft v. 8 dedicated software, running under Windows 7™.

In situ XRF

HH-XRF spectrometry is one of the most used elemental techniques in the field of cultural heritage. In the characterization of pigments, its use in combination with FORS provides a suitable approach to the preliminary identification of pigments.

Table 1 Spectral multiband imaging, overview of methods and spectra

Spectral multiband imaging method specifications	Known as	Camera			Radiation source			Complete naming
		Spectral range	Detection	Filters	Spectral range	Emission	Filters	
Reflected methods								
Visible-reflected	VIS	VIS	380–740 nm	BG38	VIS	380–750 nm		VIS-R_VIS
Infrared-reflected	IR, IRR	IR	780–1050 nm	RG830	IR	780–1000 nm		IR-R_IR
UV-reflected	UVR	UV	356 ± 10 nm	UG1 & BG38	UV	365 ± 10 nm	UG11	UV-R_UV_365
Raking light	RL	VISR	380–740 nm	BG38	VIS	380–740 nm		VISR-R_VIS
Luminescence methods								
Visible-induced infrared luminescence	IRF, VIL	IR	780–1050 nm	RG830	VIS	380–740 nm	BG38	IR-L_VIS
UV-induced infrared luminescence		IR	780–1050 nm	RG830	UV	356 ± 10 nm	UG11	IR-L_UV_365
UV-induced visible luminescence	UV Fl., UVF, UVL	VIS	420–700 nm	UV-/IR-cut L & BG39	UV	356 ± 10 nm	UG11	VIS-L_UV_365
False colour images								
IR false colour	IRFC							IRFC
UV false colour	UVFC, UVRFC							UVFC

Qualitative elemental chemical analysis of the pigments was carried out using a handheld portable Niton Xl3t X-Ray Spectrometer working at the following conditions: X-Ray tube 50KV, Ag anode 40 mA max, X-Ray detector Si Pin diode, resolution 195 eV and acquisition time 60 s. The instrumental set-up allowed for the detection of chemical elements with atomic number $Z \geq 19$ (from potassium; K).

Results and discussion

Spectral multiband imaging

An exemplary procedure is shown here, in which a concrete question is raised from results of spectral multiband imaging, prompting instrumental analysis of pigments in order to provide an explanation for the reflectance and luminescence phenomena. The SMI contributed to improve the visibility of paint layers, and in some cases, it made invisible elements visible. This was the case with the pigment Egyptian blue, which has been detected by luminescence phenomena in the IR spectrum in the monastery church of St. John in Müstair and in St. Benedict in Malles (Figs. 1 and 2). The images not only made it possible to detect the presence of a pigment which is not visible to the naked eye but also to interpret better the scenes in which it was used. In Müstair, in one area in the northern apse in which the heads of three figures and background architecture are visible, it could be shown that Egyptian blue was used in areas of the face and of the architecture where green shading would be expected (Fig. S9). It is interesting to note that no trace of this shading or of grains of blue pigment could be detected with the naked eye or with macrophotography (magnification ×100). It could be shown that Egyptian blue, possibly in combination with other pigments like ochre, was also used to add details and shades to garments. The same method of application was identified in the paintings on the eastern wall of the church of St. Benedict in Malles (Fig. S10).

The VIS luminescence images induced by UV light showed abnormalities on the surface, which can serve as a basis for metrological methods like FORS and XRF, but also provide information on the painting techniques. For the monastery church of St. John in Müstair, Fig. S11 shows a characteristic orange glow which indicates the presence of a pigment which through previous invasive sampling had been identified as *minium* (red lead). In the same church, Fig. S12 shows the head of the figure of Christ in the semi-dome of the central apse before the start of restoration work. The extent of the overpaintings from the 1947–1951 restoration campaign can be clearly seen. This information is of great help for the planning of the conservation and restoration measures.

In situ FORS and XRF analysis

A wide in situ diagnostic survey was carried out by means of FORS and XRF techniques on the paintings at the two sites. Using scaffoldings, it was possible to reach the mural paintings at a height of up to 5 m. In particular, in the church of St. John in Müstair, we analysed the paintings in the central apse, in the northern apse and in the attic; in the church of St. Benedict in Malles, we analysed the paintings on the eastern and northern wall. The results of in situ investigation are discussed in the following paragraphs.

Blue pigments

In situ FORS and XRF measurements allowed the identification of Egyptian blue and of ultramarine blue at Malles and Müstair. In the 1980s, Franz Mairinger identified both Egyptian blue and ultramarine at Müstair by means of XRD analysis carried out on samples taken from the Carolingian frescoes in the attic of the monastery church (unpublished report in the Archive of the Foundation Pro Monastery of St. John). However, the presence of ultramarine blue was omitted in a following paper (Mairinger and Schreiner 1986). Oskar Emmenegger (1998) listed ultramarine blue among the Carolingian pigments used at Müstair but without referencing the source of the information. This important fact has therefore never been fully appreciated. The renewed confirmation of the presence of ultramarine blue at Müstair (Fig. S13) is therefore an important analytical result.

Regarding the church of St. Benedict in Malles, on the other hand, the presence of ultramarine was unknown until now. The areas where this pigment has been identified seem to overlap with those in which Egyptian blue is also present. The identification of ultramarine blue in blue areas was obtained by means of FORS, while XRF yielded the presence of Cu together with Pb and Ca; considering that FORS analysis provides a response from the uppermost pictorial layers only, these results suggest that Egyptian blue or azurite (or other Cu-containing pigments) could be present in the underlying layers, below a layer containing ultramarine blue.

The presence of Egyptian blue in the two painting cycles is extremely significant, being another confirmation of the fact that the technology of production of this pigment was anything but lost after the end of the Roman empire, particularly in Italy and the neighbouring regions. In recent years, an increasing number of identifications have been reported, mainly in paintings in Italy and nearby countries (Nicola et al. 2018 and references therein). Additional information came from in situ XRF analysis: at both sites, the blue paints contained Cu only, as if the pigments were produced from a traditional recipe. By comparison, in the case of the ninth-/tenth-century mural paintings at Castelseprio (Lombardy), the Egyptian blue

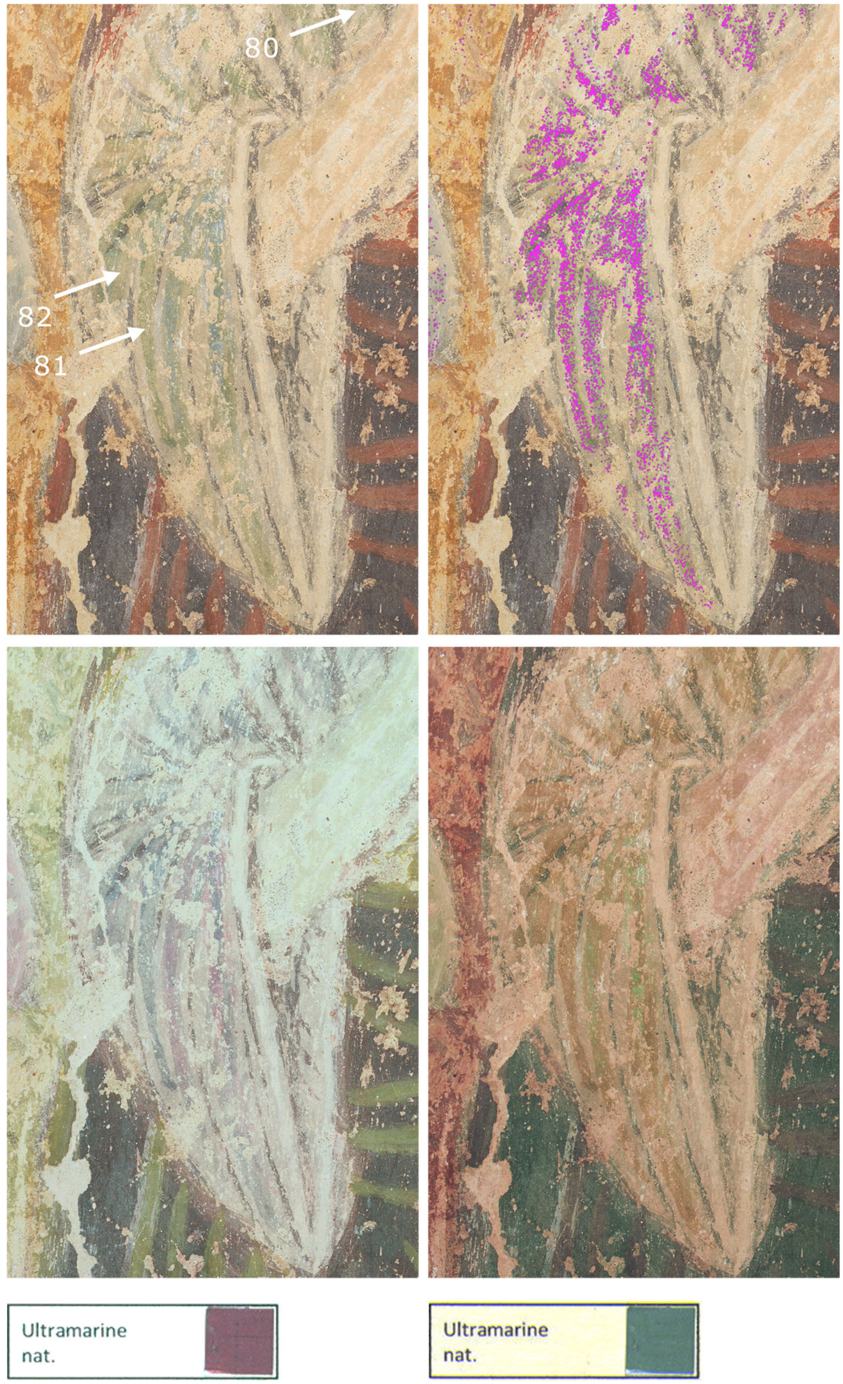

Fig. 1 Church of St. Benedict in Malles, eastern wall, central apse, Christ-figure. Detail of multispectral image with reference material for ultramarine blue from chsopensource.org. False-colour VIL superimposed on different spectra. Top from left to right, visible light, VIS superimposed on visible light. Bottom from left to right, IR false-colour, UV false-colour. The images indicate the presence of ultramarine and Egyptian blue. The location of measurements nr. 80–82 have been marked in the top left image. Photo: Annette T. Keller, artIMAGING

utilized was apparently produced from a Cu/Zn alloy rather than from Cu or bronze (Nicola et al. 2018).

The presence of ultramarine blue at Malles deserves an in-depth analysis. With in situ measurements only, it would not be possible to understand whether the pigment detected was being used in the oldest pictorial layer from the ninth century or in subsequent restoration work. The results of FORS and XRF analyses are contrasting in this case and suggest that ultramarine blue is not the first blue layer. Subsequent in-depth analysis carried out on micro samples could reveal the exact nature of the pigment, based on the size and morphology of the grains.

Green pigments

No green pigments were identified at Müstair, in agreement with the results of Mairinger and Schreiner (1986). At Malles, in the shadings of Christ's face (measurement nr. 79, Table 2), we identified the pigment green earth by means of FORS, while XRF highlighted the presence of Fe and K and also

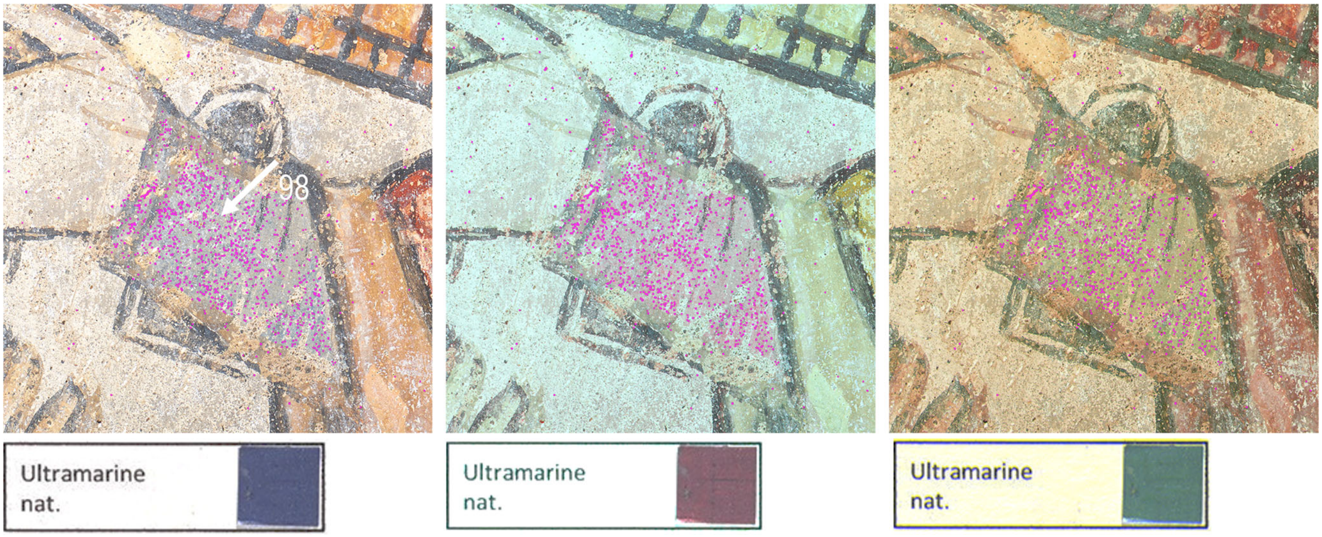

Fig. 2 Church of St. Benedict in Malles, eastern wall, clerical benefactor, detail of multispectral image with reference material for ultramarine blue from chsopensource.org. False-colour VIL superimposed on different spectra. From left to right, visible light, IR false-colour, UV false-colour. The images indicate the presence of ultramarine and Egyptian blue. The location of measurement nr. 98 has been marked in the leftmost image. Photo: Annette T. Keller, artIMAGING

Cu and Pb. The area showed a marked VIL signal, indicating also the presence of Egyptian blue.

Purple pigments

In the attic of the monastery church at Müstair, some areas today appear as a dark purple colour. In the work by Mairinger and Schreiner (1986), the authors reported "...an organic lake pigment of purple hue, surprisingly well preserved". The analysis was carried out on a micro sample by means of thin layer chromatography (TLC) which "...showed the presence of madder, although the spots were not quite convincing" (original in German, translation by the authors). In our measurements, FORS analysis yielded a spectrum attributable to an organic colourant (confirmed by the lack of key elements evidenced by XRF analysis) but definitely not identifiable as madder as can be seen in Fig. 3 a nor as another anthraquinone dye or any other purple or violet colourant (Aceto et al. 2014). The presence of madder would not be unusual in a painting from the eighth or ninth century. Its mention in the *Capitulare de villis* (Chenciner 2000), the decree issued by Charlemagne containing regulations for the cultivation of plants on the royal estates, suggests that it was in common use in Carolingian times. One hypothesis could be that an original madder layer has been subjected to fire and so turned to an altered phase of unpredictable composition. This hypothesis would find preliminary support in a FORS spectrum obtained from a dark area (Fig. 3 b) which could be identified as tenorite – CuO – an alteration phase possibly generated by copper pigments as a consequence of firing (Sotiropoulou et al. 2008). According to archaeological investigations at the monastery site, two fires ravaged the church: one in the first half of the tenth century and another around 1020 AD. Further in-depth study is needed to elucidate this point.

Red/brown/orange pigments

Mostly Fe-based pigments (red ochres) were identified for red and brown hues. We did not find evidence of the organic lake pigment identified at Müstair by Mairinger and Schreiner (1986), but this could possibly be due to not replicating the analysis in the same spots; FORS analysis is able to identify the reflection spectrum of madder or other organic colourants such as scale insect dyes.

A remarkable feature identified on both cycles is the occurrence of several grey-blackish areas which yielded the overall presence of Pb when analysed by means of XRF. The same areas showed unusual FORS spectra (examples are reported in Fig. 3 c) with a reflectance maximum at 670–780 nm and a decrease beyond 750–800 nm. This means that the pigment absorbs in the NIR region, a feature definitely uncommon among pictorial materials. Such spectral features are not compatible with any known grey or black pigment (Aceto et al. 2014). Therefore, it seems reasonable to assume an altered phase. The presence of Pb addresses the identification of the original pigment towards red lead, Pb_3O_4; white lead, $2PbCO_3{\cdot}Pb(OH)_2$; massicot, PbO; or litharge, PbO. As for the identification of the altered phase, several works in the scientific literature (Hradil et al. 2013; Gutman et al. 2018; Vagnini et al. 2018) suggest that it could be plattnerite (β-PbO_2), a product of the conversion of Pb-based pigments typically attributed to alkaline or warm conditions or, according to some authors (Rosado et al. 2016), to the action of microorganisms such as fungi, able to dissolve Pb_3O_4 and cause the

Table 2 Number of measurement points, localisation and results of FORS and XRF where IR luminescence was detected by spectral multiband imaging

Nr.	Analysed area	Spectral multiband imaging	FORS	XRF	Figure
6	Church of St. John in Müstair, central apse, scene nr. 88, symbol of St. Matthew	IRF vis-induced	Egyptian blue	Ca Fe Cu	No figure
7	Church of St. John in Müstair, central apse, scene nr. 88, symbol of St. Matthew	IRF vis-induced	Egyptian blue	Ca Fe Cu	No figure
26	Church of St. John in Müstair, central apse, scene nr. 88, mandorla at the left of Christ	IRF vis-induced	Egyptian blue	Ca Fe Cu	No figure
27	Church of St. John in Müstair, central apse, scene nr. 88, mandorla at the left of Christ	IRF vis-induced	Egyptian blue	Ca Fe Zn Cu	No figure
38	Church of St. John in Müstair, northern apse, scene nr. 104, detail	IRF vis-induced	*Minium*?	Ca Fe Pb	Figure S9
39	Church of St. John in Müstair, northern apse, scene nr. 104, detail	IRF vis-induced	*Minium*?	Pb Ca Fe	Figure S9
41	Church of St. John in Müstair, northern apse, scene nr. 104, detail	IRF vis-induced	Red ochre	Ca Fe Pb	Figure S9
42	Church of St. John in Müstair, northern apse, scene nr. 104, detail	IRF vis-induced	Red ochre	Ca Fe Pb	Figure S9
45	Church of St. John in Müstair, northern apse	IRF vis-induced	Red ochre	Ca Fe Pb	Figure S9
73	Church of St. Benedict in Malles, eastern wall, central niche, blue background	IRF vis-induced	Ultramarine blue	Ca Fe Cu Pb	No figure
79	Church of St. Benedict in Malles, eastern wall, central niche, face of Christ, green shading	IRF vis-induced	Green earth	Ca Cu Fe Pb	Figure S10
80	Church of St. Benedict in Malles, eastern wall, central niche, tunic of Christ, sleeve, green shading	IRF vis-induced, response in IRR and UVR compare well with ultramarine blue	No result	Ca Fe Cu Pb	Figure 1
81	Church of St. Benedict in Malles, eastern wall, central niche, tunic of Christ, sleeve, green shading	IRF vis-induced, response in IRR and UVR compare well with ultramarine blue	No result	Ca Fe Pb Cu	Figure 1
82	Church of St. Benedict in Malles, eastern wall, central niche, tunic of Christ, sleeve, green shading	IRF vis-induced, response in IRR and UVR compare well with ultramarine blue	No result	Ca Fe Pb	Figure 1
98	Church of St. Benedict in Malles, eastern wall, depiction of clerical benefactor, sleeve	IRF vis-induced, response in IRR and UVR compare well with ultramarine blue	Ultramarine blue	Ca Fe	Figure 2
166	Church of St. John in Müstair, church attic, eastern wall, central scene 85 with ascension of Christ, sky background left of left angel	No MSI	Ultramarine blue	no XRF	Figure S13
168	Church of St. John in Müstair, church attic, eastern wall, central scene 85 with ascension of Christ, halo of Christ	No MSI	Ultramarine blue	no XRF	Figure S13
178	Church of St. John in Müstair, church attic, eastern wall, central scene 85 with ascension of Christ, halo of left angel	No MSI	Egyptian blue	no XRF	Figure S13
180	Church of St. John in Müstair, church attic, eastern wall, central scene 85 with ascension of Christ, shading in tunic of right angel	No MSI	Ultramarine blue	no XRF	Figure S13

accumulation of Pb^{2+} ions and the subsequent recrystallisation of Pb^{4+} ions into plattnerite.

The identification of plattnerite by means of non-invasive measurements can rely on the spectrum reported by Keester and White (1969), which is, to the authors' knowledge, the only one available in the scientific literature. The authors indicated for PbO_2 an intense absorption band between 1258 and 1290 nm that is coherent with the absorption features evidenced in our FORS spectra of grey and black areas.

Unaltered minium has been identified in several places in the church of St. John at Müstair, while at Malles, the presence of red lead was only suggested by the XRF identification of Pb. In no case was a clear FORS spectrum obtained. Therefore, the overall presence of altered red and orange pigments containing Pb cannot be definitely proven.

Yellow-orange pigments

At both sites, yellow ochre was the main yellow pigment. However, we found evidence for the probable use of another yellow pigment. At Malles, some important pictorial features such as the halo of Christ and the square halos of the

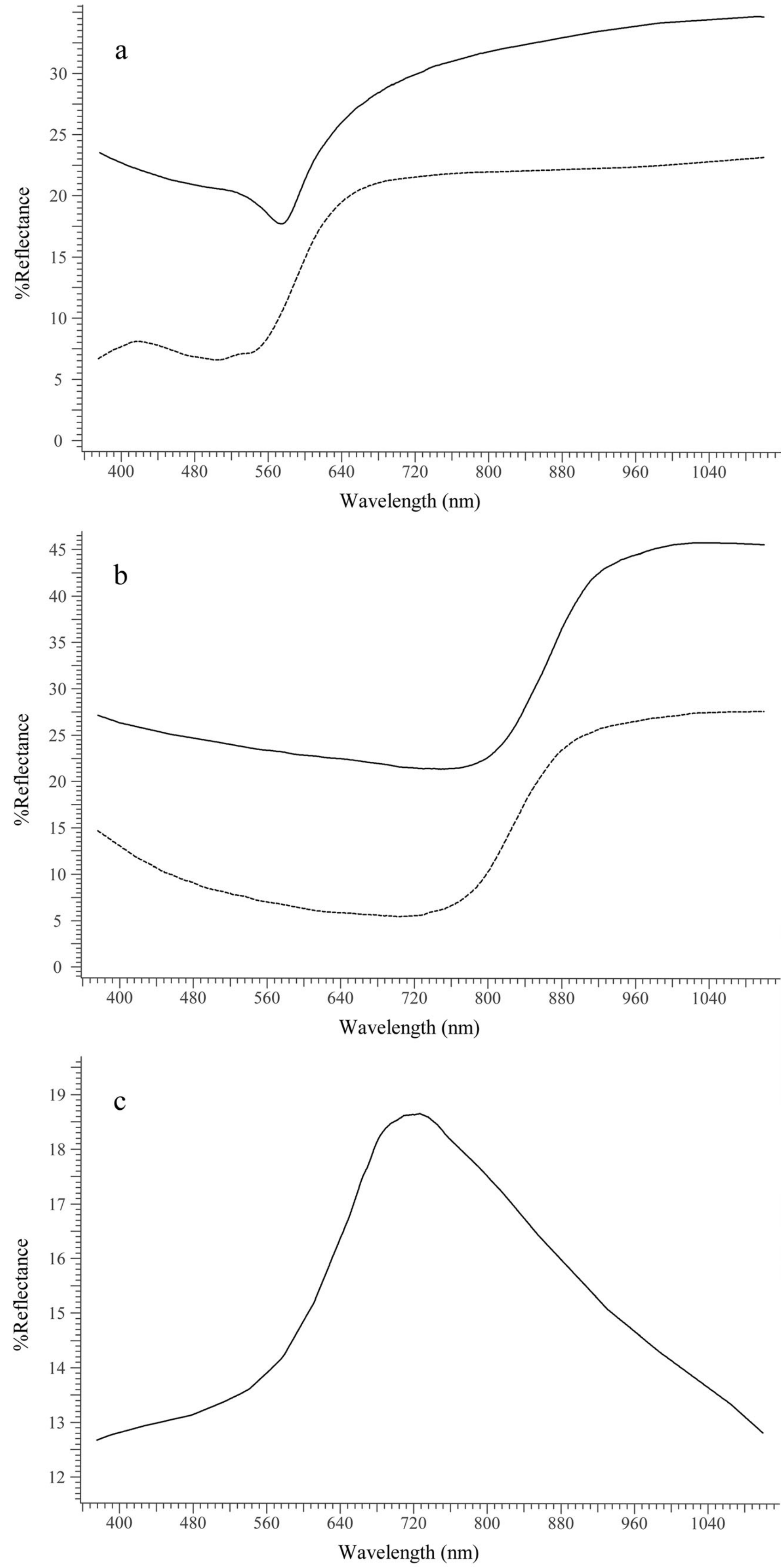
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Fig. 3 **a** FORS spectra of the purple pigment in the attic of the monastery church at Müstair (solid line) and of standard madder lake (dashed line). **b** FORS spectra of a dark area beside the purple area in the attic of the monastery church at Müstair (solid line) and of standard tenorite (dashed line). **c** FORS spectrum of a typical grey-blackish area

benefactors appeared unusually white, while they might be expected to have been of golden or at least a yellow hue. Despite FORS analysis not evidencing any coloured pigment in these areas, XRF analysis highlighted the exclusive presence of As (apart from overall Ca). These white areas also exhibit a strong bluish-white visible fluorescence under UV light (Fig. S14, Table 3, nr. 72, 74, 75, 94, 95). The presence of arsenic was also registered in the halo of Christ in the semi-dome of the main apse of the monastery church at Müstair, as well as inside the halos of two angels, which today are characterized by a red colour, identified as red ochre by FORS analysis (Fig. S12, nr. 137, Fig. 4, nr. 130, 132, Table 3). A similar result was obtained in the analysis of a Carolingian painting on the eastern gable of the Holy Cross Chapel in Müstair. At this site, a figural painting was uncovered and analysed in 2011 with XRF. Arsenic was found in different areas around the head of the figure and in an area which today appears to be of a red colour.

To explain these results, one hypothesis could be the presence of orpiment – As_2S_3 – that in St. Benedict in Malles subsequently turned to white as a consequence of alteration. Such a phenomenon was cited by Schilling et al. (2010) in their study on the wall paintings at the Mogao grotto site in Dunhuang (China); there the authors found that, while silk paintings at that site still kept the original yellow colour obtained with orpiment, most of Mogao's mural paintings, subjected to environmental exposure, had lost it, although the pigment had been identified in this and nearby wall painting cycles (Piqué 1997). Discolouring could be explained by oxidation processes (FitzHugh 1997), exposure to light (Keune et al. 2016), ozone and heat, leading to the conversion of yellow As_2S_3 to whitish As_2O_3. Other authors have suggested that microorganisms too can cause alteration of arsenic pigments (Kurek 2002).

The red ochre layers in the monastery church at Müstair could have served as underpainting for the orpiment layer which today is all but lost except for the traces of As identified by XRF.

Other pigments

A carbon-based pigment was identified for black and grey hues, and chalk – the so-called *Bianco di San Giovanni* – was identified as white pigment at both sites. These are the most typical black and white pigments in mural paintings.

Discussion

The combination of multispectral imaging with other non-invasive analytical techniques is a powerful tool for the study of pigments and painting techniques. Due to the preliminary nature of the present study, it was not possible to map systematically areas with the same spectral characteristics, as proposed by Delaney et al. (2014). The large areas involved, the varying accessibility of the surfaces and the presence of overpainting from recent restorations all restricted the possible scope of the study. Its results of the study at Müstair and Malles show that each of the technologies which have been used is limited in its scope and works best when complemented with other methods. Multiband imaging on its own provides indicative results on larger areas, which can then be tested selectively by other scientific methods – material mixtures, binders and ageing can greatly alter the spectral behaviour of materials. The great advantage of spectral multiband imaging is that surfaces may appear similar in the visible range but may behave differently in the IR and UV range. It has been shown that very precise questions and areas for further scientific investigations can be identified after the interdisciplinary evaluation of SMI. As a result, measurement and necessary sampling can be reduced to a minimum. In summary, new questions emerge out of spectral multiband imaging results. These require further analytical tools, research, interdisciplinary exchange and new approaches to image interpretation.

Among the multispectral imaging techniques, visible-induced infrared luminescence (VIL) has proven to be a particularly useful tool for the detection of Egyptian blue (Verri et al. 2010). Thanks to the application of this technique, we now recognize that knowledge about this pigment, used since antiquity, was not lost during the transition to the medieval period, as was often assumed, but persisted well into the Italian Renaissance (Verri 2009; Chiari 2018). The VIL images of the wall paintings in the monastery church of Müstair and the church of St. Benedict in Malles showed the presence of Egyptian blue in numerous places. A number of spots in areas with a strong response to VIL were chosen for XRF and FORS analysis. Table 2 shows the results of the three methods used. In less than half of the areas in which Egyptian blue had been identified by visible-induced infrared luminescence, the results could be confirmed by FORS and XRF (presence of Cu). These measurement points were located in the central apse of the church at Müstair (nr. 6, 7, 26 and 27). Five measurements did not correspond at all with the VIL result, with FORS results indicating red lead or red ochre, and the XRF not showing any presence of copper. These are all located in the northern apse of the church (nr. 38–42, 45). Additionally, ultramarine blue has been identified by MSI and FORS (nr. 73, 81–82, 98, 166, 168, 178, 180).

Table 3 Number of measurement points, localisation and results of spectral multiband imaging where the presence of As was detected by XRF analysis (trace elements in parentheses)

Nr.	Analysed area	Spectral multiband imaging	FORS	XRF	Figure
72	Church of St. Benedict in Malles, eastern wall, central niche, halo of Christ	White glow in UVF	No result	As Ca	Figure S14
74	Church of St. Benedict in Malles, eastern wall, central niche, halo of Christ	White glow in UVF	No result	As Ca	Figure S14
75	Church of St. Benedict in Malles, eastern wall, central niche, edge of halo of Christ	White glow in UVF	No result	As Ca	Figure S14
94	Church of St. Benedict in Malles, eastern wall, clerical benefactor, square halo	White glow in UVF	No result	As Ca	Figure S14
95	Church of St. Benedict in Malles, eastern wall, clerical benefactor, square halo	White glow in UVF	No result	As Ca	Figure S14
122	Church of St. Benedict in Malles, eastern wall, lay benefactor, square halo	White glow in UVF	No result	As Ca	No figure
123	Church of St. Benedict in Malles, eastern wall, lay benefactor, square halo	White glow in UVF	No result	As Ca	No figure
130	Church of St. John in Müstair, central apse, scene nr. 88, southern side, angel choir, hair of angel	No particular response	No measurement	As Ca Fe Zn (Ni, Cu, Au?)	Figure 4
132	Church of St. John in Müstair, central apse, scene nr. 88, southern side, angel choir, edge of halo of angel	No particular response	No measurement	As Ca Fe (Ni, Zn, Cu)	Figure 4
133	Church of St. John in Müstair, central apse, scene nr. 88, southern side, angel choir, halo of angel	No particular response	No measurement	As Ca Fe (Ni, Zn, Cu)	No figure
135	Church of St. John in Müstair, central apse, scene nr. 88, northern side, angel choir, halo of angel	No MSI	Red ochre	Ca As Fe (Ti/Ba, Ni, Cu, Zn, Pb, Au?)	No figure
137	Church of St. John in Müstair, central apse, scene nr. 88, halo of Christ	No particular response	Red ochre	As Ca Fe (Ni, Zn, Au)	Figure S12

At Malles, in the central niche, measurement nr. 73 showed only a partial correspondence between VIL and the other data. The FORS measurement indicated the presence of ultramarine, while XRF identified Cu on the surface. While this result could be attributed to a superposition of two paint layers, the failure to confirm the VIL data in the case of the measurements in the northern apse of the church at Müstair is unexpected. These areas were documented with macrophotography, and even with a magnification of ×100, no grains of Egyptian blue could be seen on the surface. In the northern apse of the monastery church, VIL was detected in areas belonging to the faces of painted figures where green shading would be expected. In the central apse on the other hand, where the presence of Egyptian blue was substantiated with FORS and HH-XRF, the areas can be associated with the blue background of the sky. It is therefore possible that the discrepancy of the results is due to different application methods of the pigment: in one case, it is mixed with other pigments, perhaps ochre, as shading; in the other case, it is used in its pure blue form for the sky background. The use of Egyptian blue mixed with ochre to produce a green colour was documented in Müstair in the 1980s by Franz Mairinger (Knoepfli and Emmenegger 1990, 170–171). The same use of Egyptian blue could be identified in the church of St. Benedict in Malles, where areas shaded with green paint emit a VIL signal, indicating a mixture containing Egyptian blue (Fig. S10). FORS detected the presence of green earth in these areas, which might indicate a mixture of the two pigments (measurement nr. 79, Table 2).

Another feature of the Carolingian frescoes of the monastery church at Müstair is the presence of UV fluorescence phenomena associated with specific paint layers on the surface. A characteristic yellow glow in the UV fluorescence spectrum is associated with readings of plattnerite and minium taken with FORS, while XRF measurements detected the presence of lead (Fig. S11, Table 4, nr. 30, 32, 33, 34). This yellow glow is not normally associated with minium in the comparative reference materials. In other areas, UV fluorescence photography detected a response which corresponds more closely to those given by reference materials for minium (Fig. 5), while FORS detected only red ochre, and the XRF measurements showed the presence of lead (Table 4, nr. 36, 37). Minium might therefore be present, but it has a different response under UV light to the minium detected at the points 30, 32, 33 and 34. This could be the consequence of the use of different mixtures of pigments, e.g. ochre and minium, or of

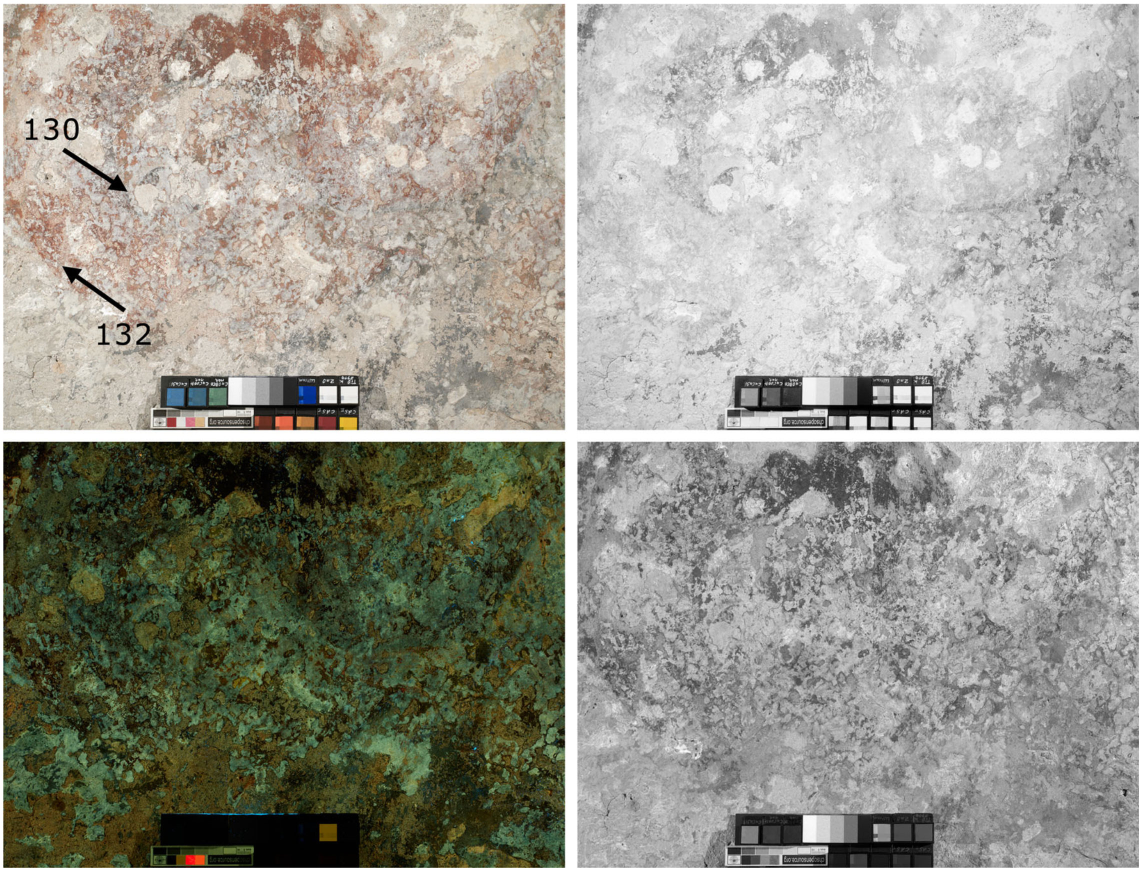

Fig. 4 Monastery church of St. John in Müstair, central apse, scene nr. 88, southern side, detail of choir of angels (angel head). Top left, visible light; top right, IRR; bottom left, UVF; bottom right, UVR. Calibration card from chsopensource.org. The locations of measurements 130 and 132 have been marked in the top left image. Photo: Annette T. Keller, artIMAGING

different binders. Since the lead pigments identified on the Carolingian frescoes in Müstair are mostly altered, FORS analysis is not very reliable in this case.

In the church of St. Benedict in Malles, a response compatible with minium in multispectral images was observed in areas which yielded no clear results by using FORS. These

Table 4 Number of measurement points, localisation and results of spectral multiband imaging where the presence of red pigments (ochre and minium) has been suggested, of FORS and of XRF analysis

Nr.	Analysed area	Spectral multiband imaging	FORS	XRF	Figure
30	Church of St. John in Müstair, northern apse, scene nr. 104, building in the background, red-grey roof	Yellow glow in UVF	Plattnerite?	Pb	Figure S11
32	Church of St. John in Müstair, northern apse, scene nr. 104, building in the background, red-grey roof	Yellow glow in UVF	Minium?	Pb Ca Fe	Figure S11
33	Church of St. John in Müstair, northern apse, scene nr. 104, building in the background, red-grey roof	Yellow glow in UVF	Plattnerite?	Pb	Figure S11
34	Church of St. John in Müstair, northern apse, scene nr. 104, building in the background, lips of a figure	Yellow glow in UVF	No result	Pb	Figure S11
36	Church of St. John in Müstair, northern apse, scene nr. 104, left figure, red hair on the left side of the forehead	Responses in various spectra compare well with red ochre	Red ochre	Ca Fe Ti	Figure 5
37	Church of St. John in Müstair, northern apse, scene nr. 104, left figure, red hair on the left side of the forehead	Responses in various spectra compare well With minium	Red ochre	Ca Fe Pb	Figure 5
69	Church of St. Benedict in Malles, eastern wall, central niche, lower edge of the book held by Christ	Responses in various spectra compare well with minium	No result	Pb Ca Fe	Figure 6
90	Church of St. Benedict in Malles, eastern wall, ecclesiastical benefactor, red delimitation on the right	Responses in various spectra compare well with red ochre	Red ochre	Ca Fe	No figure

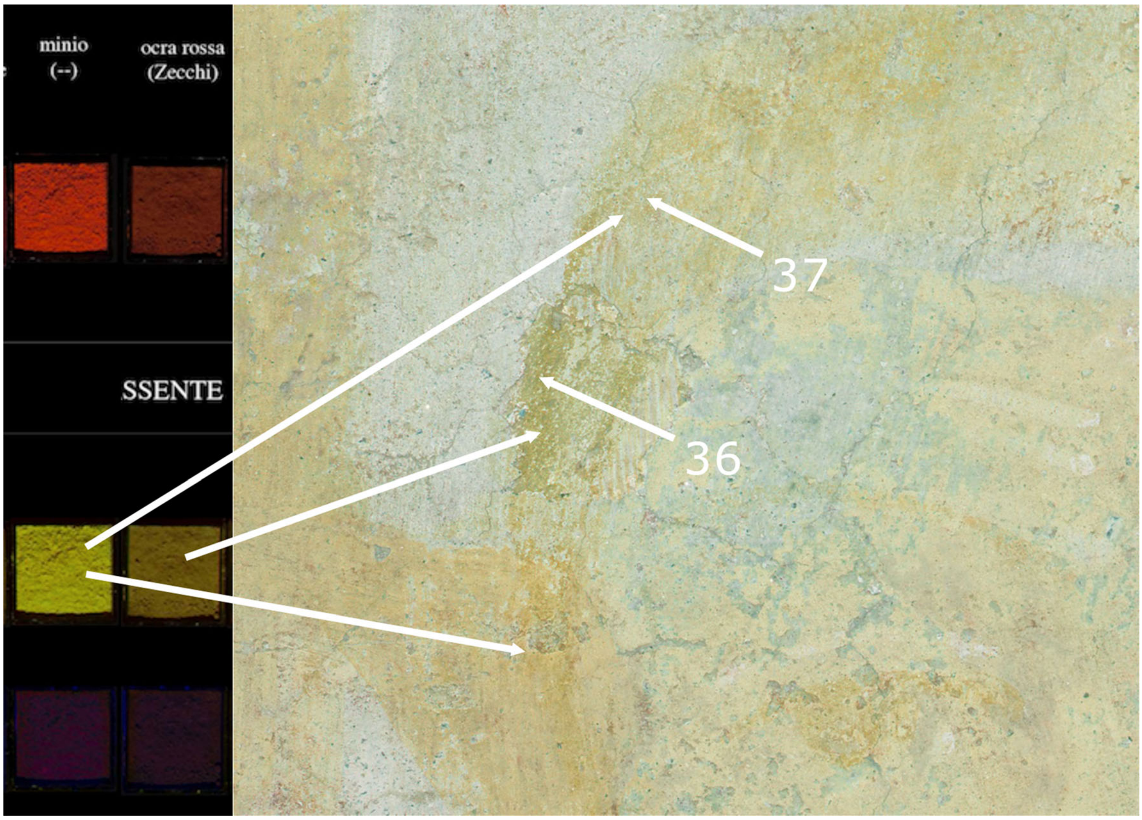

Fig. 5 Monastery church of St. John in Müstair, northern apse, scene nr. 104, detail. UV fluorescence false-colour image and reference material (left square, minium; right square, ochre) from master thesis of the Opificio delle Pietre Dure, Florence (Caruso 2009), with location of measurements nr. 36 and 37. Photo: Annette T. Keller, artIMAGING

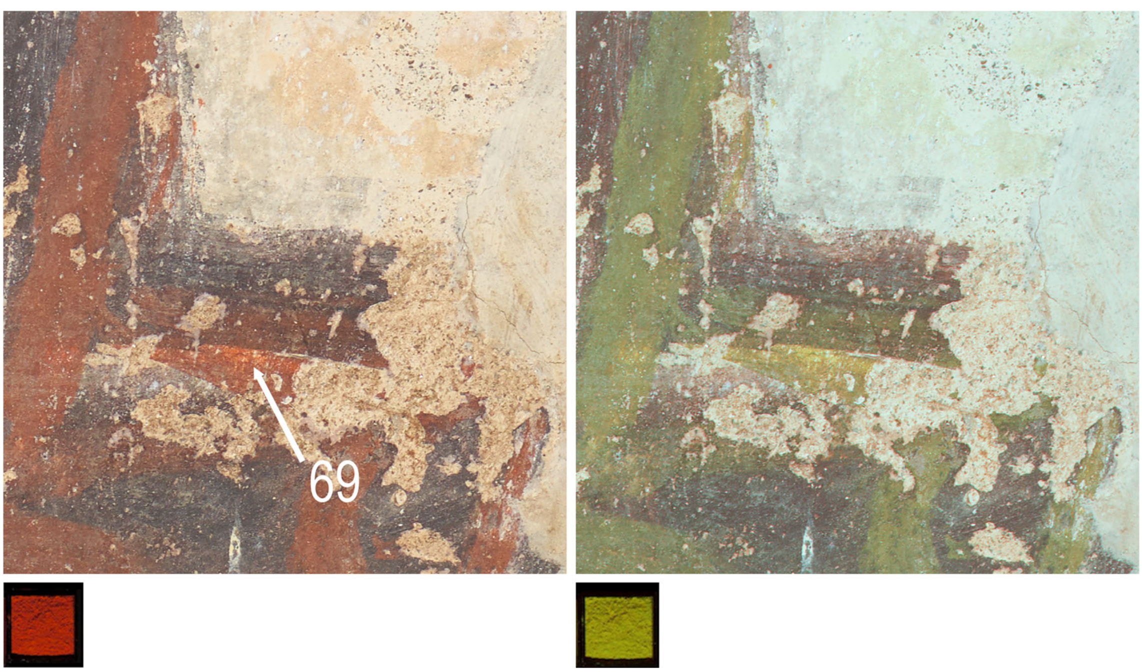

Fig. 6 Church of St. Benedict in Malles, eastern wall, central niche. Visible light image (left) and infrared false-colour image (right) with reference material for minium from master thesis of the Opificio delle Pietre Dure, Florence (Caruso 2009). The location of measurement nr. 69 has been marked in the left image. Photo: Annette T. Keller, artIMAGING

areas today have an orange-red colour, and XRF analysis detected the presence of lead (Fig. 6, Table 4, nr. 69). Also in St. Benedict, the FORS and XRF results confirmed the identification of red ochre with SMI (Table 4, nr. 36, nr. 90).

The presence of As-based pigments has been detected solely by XRF analysis. Neither FORS nor SMI give any indications as to what specific pigment might have been used (Table 3). It was most likely orpiment, but invasive sampling will be needed to identify this pigment. In three cases, As was associated with traces of Au. The significance of this result has yet to be ascertained with more precise methods.

Conclusions

Spectral multiband imaging, paired with FORS and XRF analysis, gave important insights into the painting techniques at the monastery church of Müstair and at the church of St. Benedict in Malles. There are clear similarities in the palette of pigments and the way they were used between the frescoes on the eastern wall of the church of St. Benedict and the monastery church of Müstair. The colour palette is composed of pigments typically used in mural paintings: red and yellow ochres, carbon black, *Bianco di San Giovanni* and green earth. These basic pigments are supplemented by lead pigments, which are less suited for use on plaster surfaces, lead red (probably) at Malles and lead yellow at Müstair, while lead white could not be identified with certainty at either site. For blue and green hues, mixtures containing Egyptian blue and ultramarine blue have been used.

The use of Egyptian blue and ultramarine blue puts the paintings closer to the ancient Roman than to the Romanesque tradition. The use of both pigments has recently been attested in early medieval wall paintings at Castelseprio (Santa Maria foris portas – Egyptian blue; Nicola et al. 2018), Rome (San Saba – Egyptian blue mixed with ultramarine blue; Gaetani, Santamaria, Seccaroni 2004) and San Vincenzo al Volturno (abbey church and crypt of San Giosué – Egyptian blue; Howard 2001). Both at Malles and at Müstair, Egyptian blue was used in two different ways: either as a homogenous layer for the sky backgrounds (on top of a grey or black underpainting) or mixed with other pigments to give a green hue. In the latter case, it was used to shape smaller details (globe of the angel in the central niche at Malles), as shading for human faces (edges of the faces, eye sockets, nose, cheeks, chin and neck) and for the shading of garments (at Malles) and architecture (at Müstair). While the mixing of Egyptian blue and yellow ochre to give a green colour could not be demonstrated by the methods used, the combination of VIL and FORS analysis has shown that in the central niche at Malles, Egyptian blue was used together with green earth (measurement nr. 79, Fig. S10). A different use of blue pigments is attested in the portrayal of the ecclesiastical benefactor at Malles. Here, Egyptian blue is present in areas of the face and of the tunic. These areas coincide with the distribution of ultramarine blue in the same painting, identified by SMI and FORS. These areas today appear bluish-grey (Fig. 2). A very similar use of Egyptian blue and ultramarine blue can be identified in the central niche by MSI. Here, as in the case of the painting of the clerical benefactor, ultramarine blue seems to overlap with areas painted with Egyptian blue in the sky background and the globe of the angel, as well as in the light blue areas of the tunic of Christ. MSI indicates that the ultramarine blue layer was applied on top of a green layer containing Egyptian blue (Fig. 1). FORS did not detect the presence of ultramarine blue in these areas (measurements nr. 80–82, Table 2), but the MSI images are so similar to those of the benefactor, where ultramarine blue was detected by FORS, that it is very likely that the same pigments were used. The paintings on the northern wall of the church of St. Benedict on the other hand are not only painted in a markedly different style from the figures in the niches but also lack any trace of Egyptian or ultramarine blue. Red and yellow ochre and minium were the only pigments which could be identified.

The use of Egyptian blue mixed with ultramarine blue is exceptional and has hitherto been detected only in frescoes of the first half of the eighth century at San Saba in Rome (Gaetani, Santamaria, Seccaroni 2004). With the data available, the interpretation of these observations can only be tentative. Given the results of the analysis, it seems that on the eastern wall at Malles, Egyptian blue and ultramarine blue pigments were used together, but as separate, overlapping paint layers. It cannot at present be excluded that the superficial ultramarine blue layers are a later addition. If so, it is unlikely that these stem from restoration activities, since the paintings were covered by limewash and walled up, and only uncovered again after 1914. Also, the ultramarine blue layers in some places appear to lie underneath the historic limewash layer (Fig. S15).

At Müstair, ultramarine blue was detected only on the east wall in the attic of the monastery church, inside the central ascension scene. The scene is partly covered by the later addition of gothic vaulting. In the centre, the mandorla of Christ is still visible, together with his halo and part of his head. To the left and the right, angels support the mandorla. Egyptian blue was detected inside the halo of the left angel (measurement nr. 178, Table 2, Fig. S13). Outside the halo, ultramarine blue was used for the blue background (measurement nr. 166, Table 2, Fig. S13). Two different hues of blue made from two different pigments were therefore applied next to each other. Ultramarine blue was also used for the halo of Christ (measurement nr. 168, Table 2, Fig. S13), which was therefore of the same colour as the sky behind the left angel. Ultramarine blue was also used for the shading in the tunic of the right angel (measurement nr. 180, Table 2, Fig. S13). These observations show how Egyptian and ultramarine blue were used in very different ways. Unlike at Malles, ultramarine blue does not seem to have been used mixed with Egyptian blue or to overlap areas where Egyptian blue is present.

Spectral multiband imaging, FORS and XRF confirm that the use of lead pigments, which show up as very similar anomalies in UVF images both at Müstair and Malles, was much the same on the eastern wall of St. Benedict and in Müstair. At both sites, the painters used lead pigments to highlight parts of the faces (cheek, lips, chin, eyes and ears), or for decorative bands, in this case alternating with red (or yellow) ochre. The paintings on the northern wall and the benefactors in Malles, on the other hand, show a different and more sparing use of lead pigments. No shading or highlighting with lead pigments could be detected in their case. This observation indicates a different way of conceiving and painting faces.

The lead-based pigments at Müstair and Malles are often altered and only rarely maintain their original appearance. Usually they survive as the black mineral plattnerite, which can be identified by the presence of lead, detected by XRF. The original colour in this case can only be suggested by observing the iconographic context. In the case of the two angels in the central niche at Malles, for example, the now black halos probably were painted with red lead and therefore used to appear orange-red. If massicot was used instead, they might have appeared bright yellow. It is interesting to note that sometimes plattnerite and unaltered red lead can be observed next to each other. This could be connected to different modes of application of the paint layers: in the case of the unaltered pigment on dry plaster and in the case of altered pigments on still wet alkaline, plaster. Alkalinity has been shown to be a determining factor in the alteration of lead pigments to plattnerite (Vagnini et al. 2018). This is a question which will need to be investigated further.

An exceptional and rare result in the context of early medieval wall paintings in Europe is the detection of a pigment based on arsenic. The fact that this is probably altered and/or present only in small traces has prevented the identification of the pigment. Its distribution exclusively in the halos of figures (at Malles in the halo of Christ in the central niche and inside the square halos of both benefactors, at Müstair inside the halo of Christ and of two angels in the semi-dome of the central apse) cannot be a coincidence and suggests orpiment, a vivid, yellow colour similar to gold. This use of orpiment would coincide with its use in illuminated manuscripts of the era (Brown and Clark 2004; Bioletti and Moss 2017). The association of As with traces of Au in the church of Müstair suggests that shell gold might have been added to the orpiment. The *Schedula diversarum artium*, a treatise from the twelfth century, lists three recipes for grinding gold to a fine powder for gilding (Chapter 35–36, in: Hendrie 1847, 246–253). The use of ground gold in wall paintings is attested in the fifteenth century by the Tuscan painter Cennino Cennini (Merrifield 1844, 98–99).

Even though the results presented here are preliminary and limited in scope, the differences in the use of the pigments which have been identified, especially of the blue, the red lead and the arsenic pigments, provide important elements for a better understanding of the techniques used in the paintings of the two churches and their relation to each other. It is evident that the differences in style between the paintings in the niches and the paintings of the benefactors/paintings on the northern wall at Malles are mirrored by differences in pigments and their mode of use. While the benefactors and the paintings on the northern wall have until now been considered to be stylistically closely related and therefore been attributed to the same workshop (Garber 1915; Emmenegger and Stampfer 1990; Rasmo 1981), analyses have shown some important differences, namely, in the presence of Egyptian Blue and ultramarine blue in the paintings of the benefactors and their absence in the paintings on the north wall. On the other hand, the use of minium for the modelling of the face was similar between these two groups. The significance of these differences, whether they can be attributed to different workshops and different chronology or whether they reflect the higher importance attributed to the paintings of the benefactors in relation to those on the north wall, can only be ascertained after further material and art-historic studies. Clear similarities could be ascertained in the use of pigments between the eastern wall of St. Benedict at Malles and the paintings in the monastery church at Müstair.

These first results show that the interpretation of spectral multiband imaging (macro), FORS and XRF is not a task that conservators can perform themselves, without knowing in detail the physics of each analytical method. On the other hand, the scientific data needs to be put into context. This requires knowledge of the stratigraphy of paint layers and historical painting techniques. An interdisciplinary team of experts (technicians and scientists) of different disciplines can provide the meaningful results needed.

The limits of the methodology presented in this paper are also made clear: the penetration depth of FORS is very low and the one of XRF is higher, while that of multiband spectral imaging varies, and cannot be precisely determined. Therefore, the sequence of paint layers is sometimes uncertain, and it becomes difficult to discern between original paint layers and later additions or restorative interventions. Sections of samples taken from the painted surfaces can provide this missing information. However, the described non-invasive in situ analytical techniques have the potential to answer many questions regarding painting techniques and pigments and therefore minimize the necessity of such invasive sampling. They are also an important tool for developing working hypotheses which may then lead to an informed and efficient sampling strategy.

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Authors' contributions All authors contributed to the conception and design of this study. P. Cassitti and L. Villa composed the historical framework and the archaeological and artistic sections; R. Emmenegger, S. Wörz, L. Villa and P. Cassitti are responsible for the sections concerning restoration and provided technical documentation; G. Cavallo, A.T. Keller, R. Lenz and M. Aceto carried out in situ measurements. All authors discussed the results of the diagnostic campaign. The first draft of the manuscript was written by P. Cassitti, and all authors commented on preliminary versions of the manuscript. All authors read and approved the final manuscript.

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