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PAINTING LAYERS ON STONE: STUDY OF AN EARLY MIDDLE AGES HIGH-RELIEF

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ABSTRACT
Examples of painted layers on statues, bas-reliefs and other architectural elements have been discovered in the course of conservation works in last decades. In most of the cases painting layers are in the state of remnants because of decay mechanisms, soiling, and invasive cleaning. Nevertheless, these colour relics witness ancient pictorial techniques, and contribute to define a symbology, an iconography, and the importance of stone elements in a complex building. An important high relief representing the figure of St. Siro, who is traditionally said to have been the first bishop of Pavia during the 1st century, but probably lived during 4th century, is conserved in Sts. Gervasius and Protasius Church in Pavia.

The high-relief, a limestone slab of about 116 x 49 cm, was covered by a lime wash light-brownish in colour, probably imitating other stone elements in the Church façade, at the center of which the sculpted slab was embedded in the masonry till 1861. After then the slab was recovered in an inner chapel where conservation works were recently carried out, taking the staring point for an analytical survey.

A careful cleaning, carried out with distilled water heated up to 30 °C, highlighted the presence of polychrome surfaces, which have been analysed by means of optical microscopy, SEM-EDS, and Micro-Raman (μRaman) techniques with the aim to characterise both pigments and grounds. Moreover, a petrographic characterisation allowed to identify the nature of the stone substrate.

The data obtained will be used by archeologists and art historians to understand better the provenance of the San Siro high-relief. Actually, it could be hypothesized that it comes from late Roman period, having been re-used during early middle ages centuries, when it was partially re-sculpted and painted.

INTRODUCTION
A high-relief representing the figure of St. Siro, located in a chapel dedicated to this saint in the church of Sts. Gervasio and Protasio in Pavia (in Lombardy region – Italy), has been recently subjected to a careful restoration intervention. The high-relief, consisting of a single piece of stone, which is 116 cm high, 49 wide and 20 cm deep including 3 cm of a background slab, was covered with light-brownish lime wash layer that hampered the legibility of the artwork. This layer was removed by gentle swabbing with the tepid water (30 °C). The restoration revealed an almost integral polychromy applied on the stone elements. San Siro is depicted here wearing a tunic of orange, red and green tones, with a crosier in the right hand and a prayer book in the left hand (Fig. 1).

The importance of systematic studies on polychrome stone works has been already pointed out in some papers dealing with decorated architectural elements and bas-reliefs all over Europe and especially in France [2, 14, 15] and Italy [11, 13]. Recently polychrome remnants has been recovered and studied in the basilica of St. Ambrogio in Milan [4], which is very close to the town of Pavia. The two Saints Ambrogio and Siro are linked by common historical events, through the Saints Gervasio and Protasio, who is dedicated the church in which the bas-relief is conserved.

There is a lack of published research surveys, which does not yet allow a profound comparison of the techniques and/or materials utilized for the polychrome decoration. On the contrary the application of painting layers to sculpted stone was a diffused practice and played a great role in Romanesque and Gothic architecture. Unfortunately remains of the original painting layers on sculpture is scarce due to natural weathering, pollution, unsuitable restorations treatments; in the specific, cleaning techniques could be responsible for the loss of painting layers. Moreover conservation works as well as the change of taste and re-use, often led to repainting as in this case.

Fig. 1: High-relief of San Siro statue in Pavia before and after the restoration

A careful stylistic observation of this statue, evidenced some particular characteristics of the working technique. In the specific, a simple working of the face, obtained by few and distinct taps of large edge chisel is appreciable. On the other hand, the working style of the vestment and even the one of the hair is more elaborated. The hair style rendering is precise, well-ordered and more authentic. In fact, during a closer examination of the area between the hair and the face, it is possible to distinguish a disproportionate step as if the hair were worked out from another existing part; moreover, the position of the right forearm and its attachment to the body is rather unnatural, probably because of the will to insert the bishop's crosier and lack of the space in the limestone slab. In fact, later in time, the author was constrained to form the right shoulder 5 cm narrower with respect to the left one. The forced choice was well masked by the refined and rich robe folds on the right shoulder.

The stylistic contrast between the plasticity of the and the rigidity of the drapery suggests that an antique Roman "provincial models" sculpture from III century was re-elaborated and painted in XI-XII century. This hypothesis is in tune with the advancement and transformation of medieval sculpture from figurative high-relief towards autonomous statue and from the simplification of the forms towards the recovery of the realistic representation, that flourished specifically in that period in Lombardy region.

These peculiarities arouse the desire to understand and analyse the nature of materials constituting the rediscovered polychromy. This task has been assigned to the authors by the authorities of Cultural Heritage Superintendence of Milan and is object of this paper.

EXPERIMENTAL SECTION

Analytical Techniques

Micro-fragments of the samples were observed with Leitz Wild M420 stereomicroscope; polished cross-sections were observed in reflected light using a Leitz Ortholux microscope with Ultropack illuminator; both microscopes were equipped with a digital image capturing system. BSE images, X-ray maps and micro-beam analyses were collected with a JEOL 5910LV scanning electron microscope equipped with X-ray spectrometer IXRF Systems/EDS 2000.

The analyses were carried out on polished cross-sections following graphitization. The EDX qualitative spectra of squared areas or spots and elemental maps were registered from 0 to 20 kV and at $1–3 \times 10^{-7}$ A.

Raman spectra were obtained using a Renishaw 2000 Raman microscope system. An Argon ion laser excitation source emitting at 514.5 nm at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} was employed for the analysis of green pigment, while for the red and blue pigments a laser at 785 nm (diode laser) was utilized. Acquisition of the spectra was carried out by using the highest magnification objective (50 x) and multiple accumulations in order to improve signal to noise ratio. The instrument was calibrated using a 520 cm^{-1} line of a silicon wafer. The spectra were recorded on the surface of the loose samples available for the analysis and were not subjected to any corrections such as smoothing or baseline subtraction.

Analytical Results

Eight samples coming from painting layers (SS1-SS8) and one sample for the identification of lithotype (SS9), were sampled in different areas of the statue as described in Table 1, were main analytical results have been summarised.

Sample description	Sample color	Analytical results	
		SEM/EDX	µRaman spectroscopy
Background of the head	SS1 Reddish/ dark blue	mortar instead of stone support ground layer: magnesium lime paint layer: presence of Fe, Al and Si	sporadic crystals of ultramarine blue, calcium carbonate, carbon black, weddelite
Flesh-coloured layer	SS2 Red/brown	magnesian lime binder; Fe and Pb in the pigments	red ochre, carbon black, weddelite
Chasuble	SS3 Red/brown	pigments: presence of Fe, Al and Si	red ochre, carbon black, weddelite, calcium carbonate
Dalmatica	SS4 Green	lime binder; presence of Ca/Mg in a matrix made with Al and Si compounds; pigments: Cu co-existence with S and Cl	brochantite, minor phases atacamite and malachite, moolooite (hydrated copper oxalate), weddelite
Spine of the prayer book	SS5 Green	lime binder; presence of Ca/Mg in a matrix made with Al and Si compounds; pigments: Cu co-existence with S and Cl	brochantite, minor phases atacamite and malachite, moolooite (hydrated copper oxalate)
Dark band in the crosier	SS6 Grey/black	lime binder with Al and Si compounds; P in the pigment	carbon black, weddelite
Pallium in the upper part of chasuble	SS7 Red/pink	lime binder with Al and Si compounds Fe, P and Pb in the pigments	high fluorescence background, weddelite, calcium carbonate, gypsum red ochre and carbon black
Dark area in the band of pallium	SS8 Black	Ag	carbon black, weddelite
Stone fragment from the boarder of the slab	SS9 Stone substrate	Petrographical analysis: coralline limestone	

Table 1: San Siro statue: characteristics of the examined samples

Substrate Description

A petrographic survey demonstrates that the stone has a honeycomb pattern with drusy sparry calcite cement as is illustrated in Figure 2. Such texture are associable with the calcareous rocks made of reef-forming organisms. The provenance of the stone material is, at the moment, unknown, but it does not match any calcareous stone, quarried in the present day territory of Lombardy.

Stratigraphic study of paint layers did not evidence the presence of any ground layer. The paint layers were applied directly on the stone elements, often using magnesium lime binder. The paint layers are, on average, 50 µm thick and probably contain tiny fragments of alumino silicates.

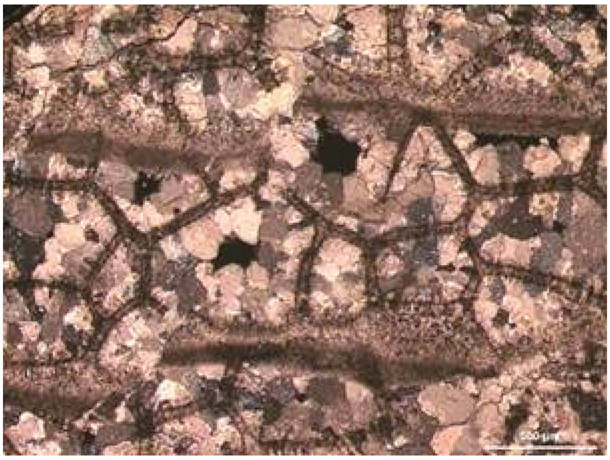

Fig. 2: Optical microscopy in polarized light, + Nicols

Pigments Description

Red brownish colour – samples SS1 and SS3

The paint layer SS1, sampled in the background behind the Saint's head, is very atypical for several reasons. The paint layer is not applied directly on the stone as for other samples but on the plaster made of magnesian lime containing alumino silicates clasts. This sample is the only case, as regard St Siro statue, in which a white ground layer (magnesian lime) is present, but as is possible to see by X-ray elemental map (Fig. 3), this portion of the sculpture is not made of limestone, but probably belongs to an insert made of a silicate rock. Moreover figure 3 showed that the red paint layer contains iron, which is attributable to red ochre, but its quantity does not seem to completely justify an intense red hue. Other element markers for red pigments such as mercury were not detected. Raman spectroscopy confirms the presence of red ochre.

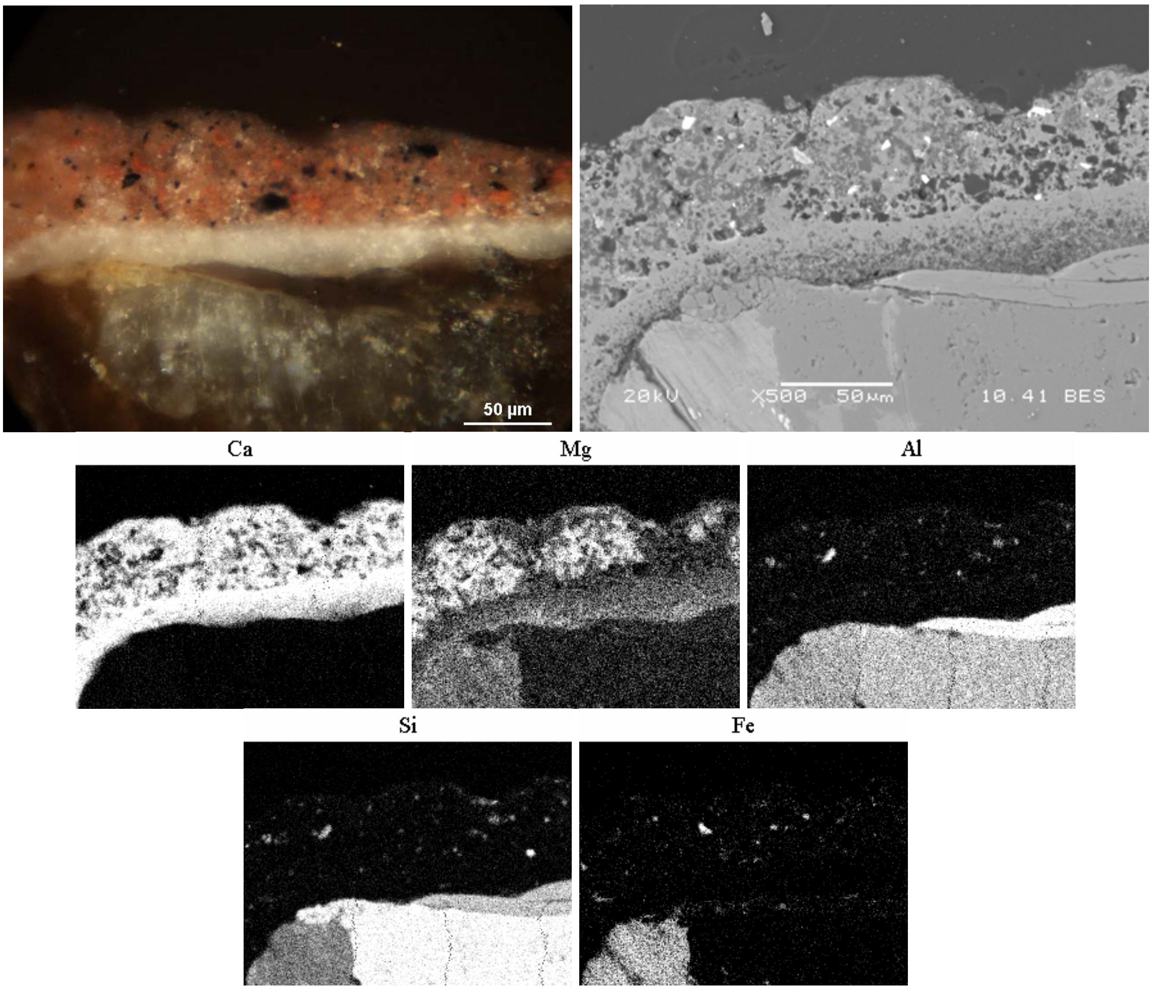

Fig. 3: Sample SS1. Polished cross section, BSE image, EDX maps of the elements Ca, Mg, Al, Si, and Fe

During the microscopic examination of SS1 paint layer, rare blue grains were found. The Raman spectrum of these blue particles corresponds to ultramarine blue (Fig. 4); a very characteristic band at 546 cm^{-1}, which has been assigned to symmetric stretching mode of the S_3^- ion, is clearly visible [1]. It has been shown previously, that these sulphur anions trapped in the aluminium silicate cage, give origin to the hue of this pigment [5].

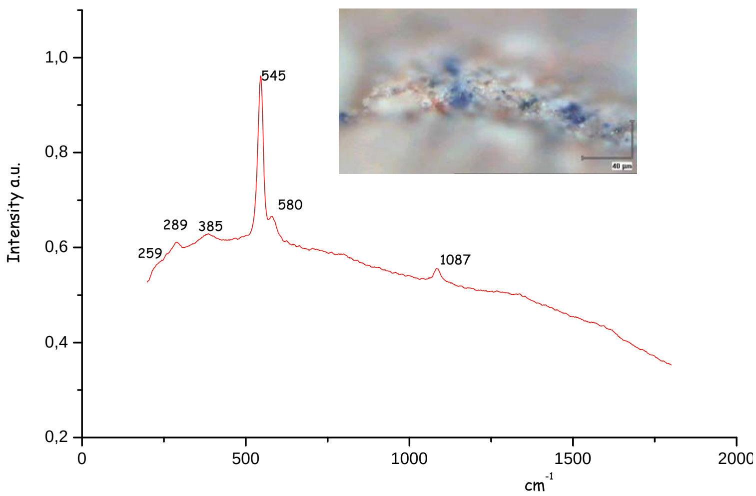

Fig. 4: Raman spectrum of blue particles

The red paint layer of Saint's chasuble, sample SS3, on the contrary respect to SS1 sample, has been directly applied on the stone substrate. The EDX elemental mapping shows the co-existence of iron, aluminium and silicon, that would suggest the use of clay containing iron oxides (Armenian bole). Raman analysis proves the employment of red ochre on the basis of the bands in low wave-numbers region at 223, 293, 409, 502, 607 cm^{-1} that correspond to the mineral hematite (α-Fe_2O_3) [1] and suggest the use of its as a red pigment. The intense fluorescence of the same red zones could suggest some organic substance that could intensify the red tones (the presence of red lakes can not be excluded). In depth analyses are currently in progress.

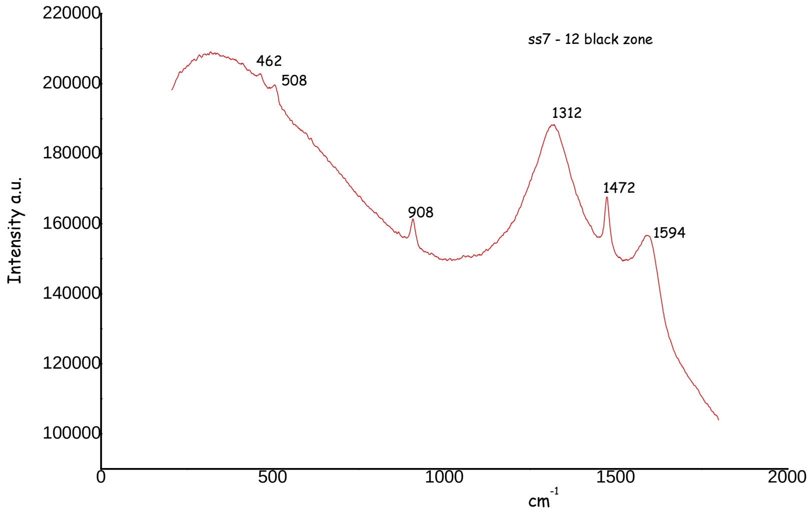

Fig.5 : SS7 Raman spectrum of black particles

For darker hue of the red colour, carbon black, was mixed with red ochre. The presence of carbon particles is proved by two broad Raman signals at 1603 and 1311 cm^{-1} [1]. Presence of black particles was verified in samples SS1 (see Fig. 5), but even in the grey/black samples SS6, SS8; in particular EDX spectra highlighted the presence of phosphorus in sample SS6, and of silver in SS8 (Fig. 6).

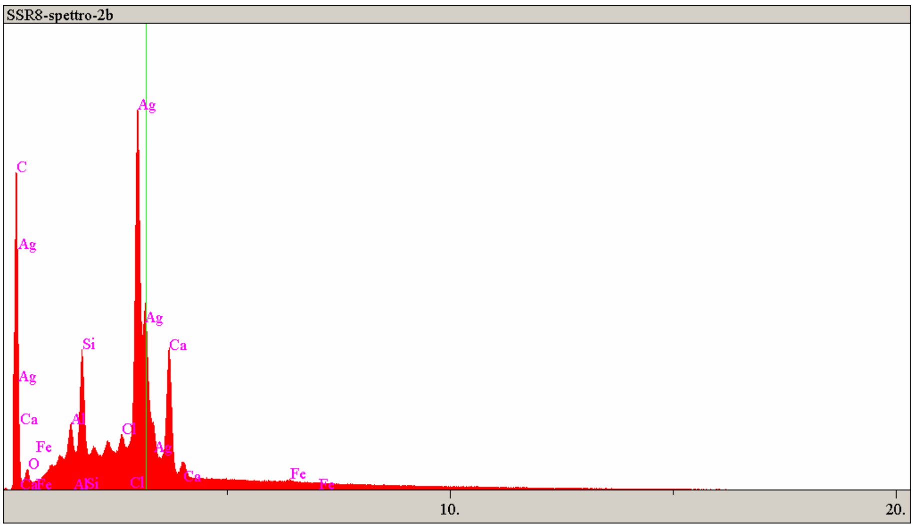

Fig.6: SS8 EDX spectrum of black area

Also weddelite (tetragonal dihydrate Ca-oxalate) was encountered throughout the whole polychromy and could be significant of mineralization of some previously present organic compounds as a binder. In Raman spectra these compounds are evidenced by the C-O and C-C stretching modes at 1472 cm^{-1} and at 910 cm^{-1}, respectively [10].

Green colour – samples SS4 and SS5

The green color is associated with samples taken from dalmatics (SS4) and the spine of the prayer book held in the Saint's left hand (SS5). In Christian symbolism this color is used to represent the triumph of life over death and is a liturgical color for specific periods. The samples demonstrate rather similar characteristics. The stratigraphy analysis reveals that the pigment, mixed with calcium and magnesium containing binder, was applied directly on the stone support. The elemental analysis unveils the presence of copper, sulphur and chlorides throughout the paint layer (Figure 7).

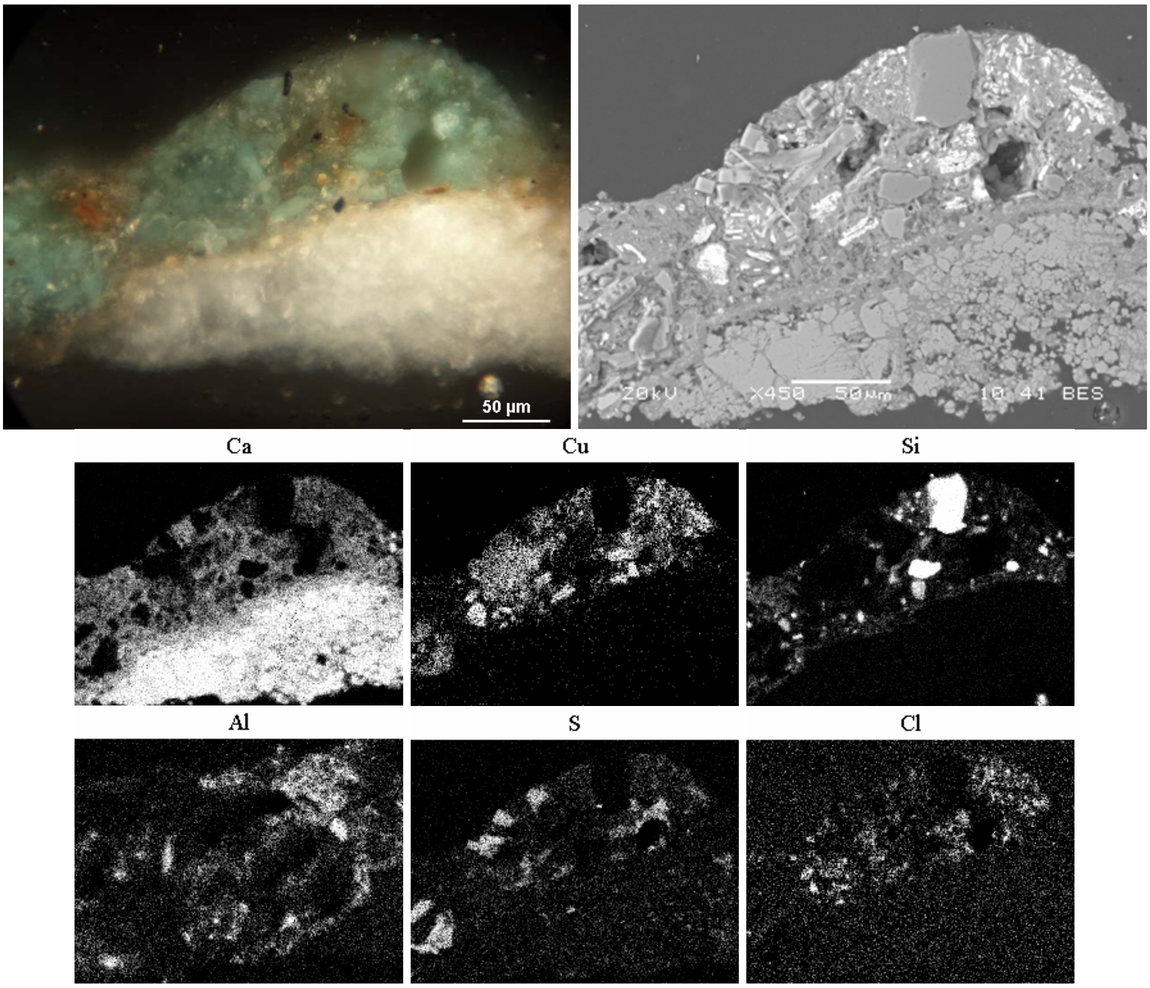

Fig. 7: Sample SS4. Polished cross section, BSE image, EDX maps of the elements Ca, Cu, Si, Al, S, and Cl

Copper with high amount sulphur suggest the presence of copper sulphates. Antlerite $CuSO_4{\cdot}2Cu(OH)_2$ and brochantite $CuSO_4{\cdot}3Cu(OH)_2$ or posnjakite $CuSO_4{\cdot}3Cu(OH)_2{\cdot}H_2O$ and langite $CuSO_4{\cdot}3Cu(OH)_2{\cdot}2H_2O$ are among the most common copper sulphates relevant to presence or corrosion of copper-containing compounds. Raman spectroscopy allows identifying of various types of basic copper sulphates, mainly by means of the position of O-H and S-O symmetric stretching vibrational modes. In the spectra (Fig.8) acquired on the green zones of sample SS4 and SS5, a strong band typical of brochantite $CuSO_4{\cdot}3Cu(OH)_2$ S-O symmetric vibration at 973 cm^{-1} was observed. Additionally, bands of the SO_4 bending region observed at 423, 448, 483, 507, 593, 610cm^{-1} and two OH symmetric stretching bands at 3585 and 3563 cm^{-1} are also in good agreement with those reported in the literature for brochantite [3, 8, 12].

The spectra of these green grains were quite complex. Apart from the bands attributable to brochantite (195, 242, 318, 367, 392 cm^{-1}), additional bands at 1514 and 1484 cm^{-1} were detected, suggesting presence of oxalates. Raman spectroscopy has already proved useful in characterization of many different oxalate compounds [10] due to the cation dependence of the CO symmetric stretching vibration bands. In fact, the signals at 1514 and 1484 cm^{-1} of the non-equivalent CO stretching vibrations are attributable to moolooite (hydrated copper(II) oxalate - $CuC_2O_4 \cdot nH_2O$, n<1) [5].. Moreover, the presence of copper oxalate was confirmed by a signal at 559 cm^{-1} (C-C-O bending and Cu-O stretching vibration modes) [9]. The region of 3200-2800 cm^{-1} proved to be useful in identifying different organic substances by means of Raman spectroscopy. A weak signal present in these spectra could suggest its presence but it is not resolved enough in order to completely understand its origin.

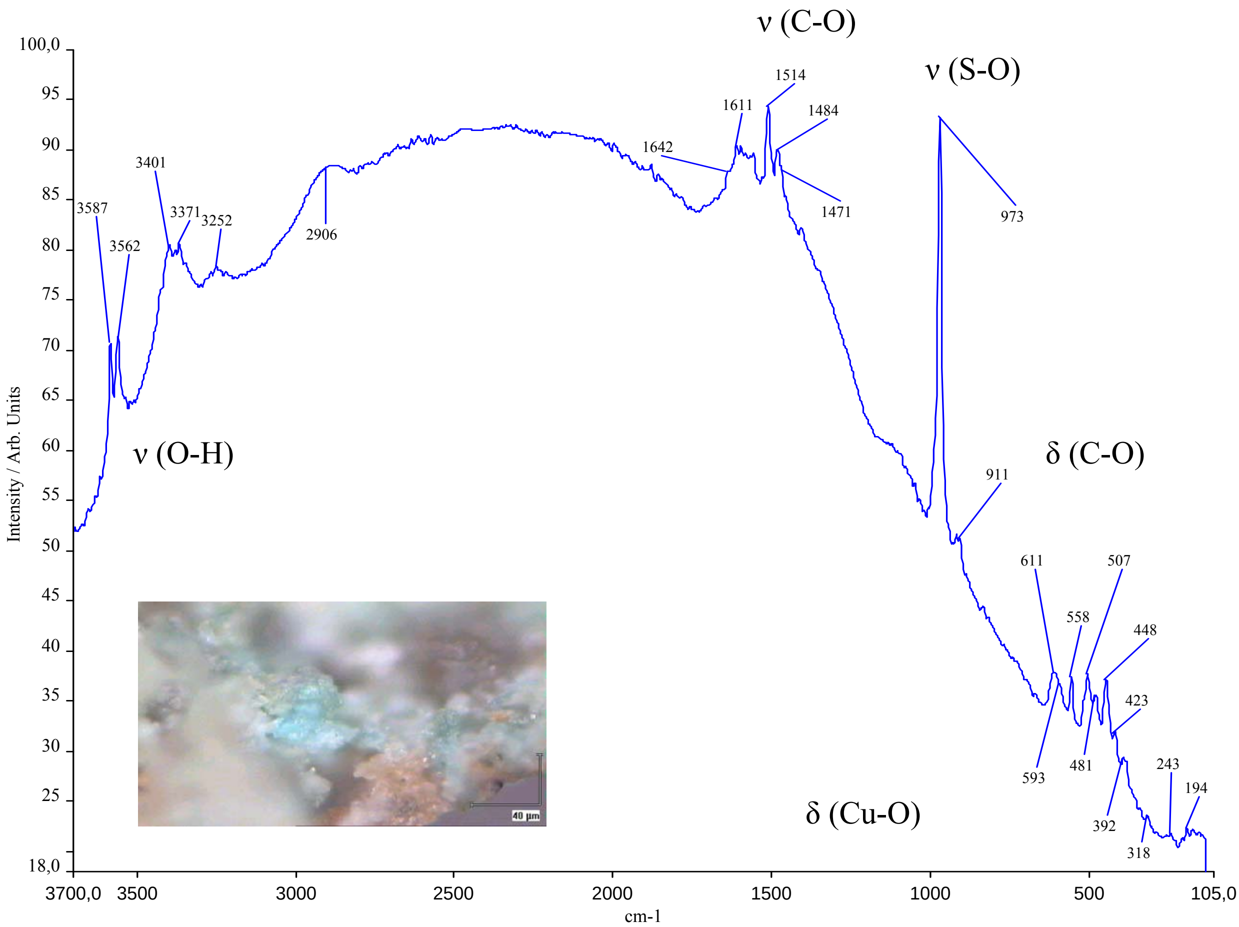

Fig.8 : Raman spectrum of green particles

In other spectra obtained in different light green zones of the same samples, the signals of another two copper compounds were observed. The complexity of these spectra suggested the co-existence of two phases: (1) basic copper chloride – atacamite (OH symmetric stretching bands at 3437 and 3356 cm^{-1} and intense 511 cm^{-1} of Cu-Cl and Cu-O band), and (2) malachite (the most characteristic bands at 430 cm^{-1} and 1490 cm^{-1} - antisymmetric carbonate vibration). To summarize, green zones of samples SS4 and SS5 are formed prevalently by brochantite with basic copper chloride (probably atacamite) and malachite as a minor phases.

Both brochantite and atacamite have been reported to have been employed as pigments [7] even though an evidence of primary utilization lacks. In these samples, their co-existence and signals attributable to malachite may suggest that their presence may also result from the alteration of the more common pigment - malachite.

CONCLUSIONS

The limestone provided a smooth surface on which painting layers, have been directly applied, avoiding the use of a ground layer. Anyway the provenance of the lithotype must be searched out of the building stones quarried in the Lombard Prealps and the Apennine. This consideration could be interesting in the reconstruction of the history of the slab; in fact archaeologists suppose a re-sculpting work of a former relief coming from Aquileia (about 260 km east of Pavia).

Comparing this high-relief with a polychrome bas-relief found on the exterior of basilica St. Ambrogio in Milan, we can find one and only analogy: the use of red ochre. In Milan Basilica, the ground layers have been detected; moreover the materials used for the green and blue color are different in the two cases: green earth and azurite in Milan and copper-based green pigments and ultramarine blue in Pavia. These findings are quite interesting, considering that the two towns belongs to two very close towns.

The ubiquitous presence of oxalates (weddellite or mooloolite) could witness the process of a complete mineralization of an organic binder, formerly present. The complexity of the composition of the green layers could be ascribed to decay processes occurred on a malachite layer, which produced basic copper sulphates and chlorides. It is necessary to remind that, as the local historical sources witness, St. Siro high-relief was embedded in the façade masonry till 1861, where outdoor environment interacted with the original pigments, leading to the compounds nowadays detected.

Anyway the compositional analyses carried out on painting layers, revealed a refined palette, comprehensive of ultramarine blue and silver, possibly present as metal powder. The presence of the lime-wash does not induce authors to suppose any recent re-painting with modern pigments. Moreover mixing ultramarine blue in a red ochre layer is, in author experience, quite unusual and remarkable.

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