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The mural paintings of Ala di Stura (Piedmont, Italy): a hidden treasure investigated†

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In the small mountain hamlet of Ala di Stura (Piedmont, Lanzo Valleys), a large but relatively unknown artistic heritage is present, made of 110 mural paintings divided among meridians and paintings with religious themes. These artworks are datable among XVI and XXI century. To support the work of touristic promotion carried out by the Commune of Ala di Stura, micro samples have been withdrawn from the most relevant artworks in order to execute Raman and scanning electron microscopy with energy-dispersive X-ray (SEM-EDX) analysis and to have useful information concerning conservation, dating and global knowledge on the artworks themselves that are little known outside Piedmont. Analyses allowed to elucidate phenomena of chromatic alteration (changing of lead pigments), to individuate pigments acting as time markers (synthetic ultramarine blue, arsenical green pigments) and to have information on the origin and exploitation of pictorial materials used by the artists who worked in Ala di Stura. Of particular interest is the fact that all pigments identified in the older paintings, and many among those identified in the newer ones, could be derived from minerals sources present in the Lanzo Valleys, among which is olivenite, a rare copper arsenate used as a green pigment that has rarely cited in the scientific literature. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: meridians; Piedmont; degradation; olivenite; microinvasive analysis

Introduction

The small mountain hamlet of Ala di Stura is located at 1080 m above sea level in the Lanzo Valleys, a group of three nearby valleys (named respectively Viù, Ala and Grande) in Piedmont region, in the north-western part of Italy. It has nearly 500 inhabitants. Ala di Stura owns a remarkable art treasure: dispersed among its 17 fractions, 110 mural paintings are present on walls of private houses, churches and chapels. The paintings are divided into paintings with religious themes and meridians. They are datable in the range XVI century–present day, with paintings dating generally older than meridians. Although the presence of meridians is usual in mountain architecture, their quantity is nevertheless surprising, making Ala di Stura the site with the highest number of meridians per inhabitants all over Europe.[1] Moreover, the wide presence of paintings witnesses the deep religious feelings of mountain people.

To make this hidden treasure known to visitors outside the valley, in 2007 the Commune of Ala di Stura started a project in order to organise and spread information on its heritage.[1] Systematic classification of the artworks was performed and updated on the basis of a previous architectural research dating to 1992;[2] this information was used to prepare paths equipped with notice boards inside the different fractions.

It was quickly apparent, although, that many of these artworks needed restoration interventions caused either by the severe atmospheric conditions typical of a mountain location with heavy annual precipitations, and by the relative carelessness of the inhabitants. It was therefore decided to investigate the conservation emergencies from a scientific point of view, performing chemical analysis on the most relevant artworks. This research project aimed also to improve the artistic–historical knowledge on the artworks collection. Diagnostic investigation was directed to address the following three major issues:

- identification of alteration phenomena occurring on paintings in order to suggest proper restoration interventions;
- improvement of knowledge on the pictorial materials used by artists and their relationship with local raw materials: Ala di Stura is located inside a mountain area rich in minerals, that is why painters could have different pigments at their disposal; and

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- a more accurate dating of artworks, by identification of pigments acting as *time markers*.

Because *in situ* analysis was hard to perform due to the difficulty in reaching most of the artworks with portable instrumentation, it was decided to proceed to micro samplings. A total of 35 among the most valuable artworks were sampled and analysed in laboratory with Raman spectroscopy; in some instances, scanning electron microscopy with energy-dispersive X-ray (SEM-EDX) analysis was used to add semi-quantitative information.

Experimental section

Samples from the 35 selected artworks were taken in variable number in order to allow characterisation of the full palette of every artwork. Sample withdrawal was performed in collaboration with an expert restorer. Samples were analysed as such, without any manipulation.

Raman spectroscopy

The Raman spectra have been collected with a high-resolution dispersive Horiba (Villeneuve d'Ascq, France) LABRAM HR model spectrophotometer equipped with a confocal microscope. The instrument is equipped with 633 nm excitation laser, 600 and 1800 lines/mm dispersive gratings, 800 mm path monochromator and a Peltier cooled charge coupled device detector. The optical arrangement on the instrument gave a spectral resolution of about 2 cm^{-1}. Spectra have been taken placing books on the microscope stage and observing them with long working distance 20×, 50× and 80× objectives. The sampled area was identified and focused using either a video camera or microscope binoculars. Exposure time was 1–120 s according to needs. The system is managed with LabSpec 5 software running under Windows XP.

SEM-EDX spectroscopy

Scanning electron microscopy images at different magnification were recorded on a Quanta 200 FEI (Hillsboro, Oregon), Scanning Electron Microscope equipped with EDAX (Mahwah, New Jersey) EDS attachment, using a tungsten filament as electron source at 20 KeV. The instruments were used in E-SEM mode (90 mbar of water pressure in chamber) in order to avoid samples metallisation.

Results and discussion

Complementary diagnostic information obtained with Raman and SEM-EDX analysis allowed to fully characterise paints, identifying not only pigments but also accessory mineral phases accompanying the main colourant phase or the preparation layers.

Identification of chromatic alteration phenomena

From the conservation point of view, apart from evidences of mechanical stress on some artworks, different chromatic alteration phenomena have been identified. The darkening of pigments containing lead was noted in two occasions. In Fig. 1, an image of Sant'Antonio (painting no. 44A, Pian del Tetto fraction) is shown, in which the face of the Saint has apparently turned from white to the present grey, which definitely cannot be the original hue on an iconographic basis. At first sight, one should expect to find evidence of conversion of lead white – $PbCO_3\,Pb(OH)_2$ – to galena – PbS – according to the mechanism already described by Clark[3] on miniature paintings. A preliminary elemental analysis performed by micro-X-ray fluorescence spectrometry gave misleading results, as it suggested the presence of Pb and S, but being K_α line of sulfur very close to M_α line of lead, the identification of PbS on this basis is far from reliable. In fact, galena was not identified at any instance with Raman analysis. On the other hand, it is reported in the literature[4,5] that laser irradiation of galena can lead to its conversion to lead oxides or oxysulfates; in this case, although the presence of lead white from the white particles of the sample was evidenced, Raman analysis yielded no evidence of any lead compound from the black particles that impart the macroscopic grey colour to the Saint's face. In fact, a Raman spectrum recorded at 0.3 mW laser power (Fig. 1) suggested a biological source according to bands occurring at 1259, 1310, 1340, 1523 and 1600 cm^{-1}, which recalls the biodiagnostic signature cited by Edwards *et al.*[6] In this Figure, the spectrum obtained at full laser power is reported also, which seems to suggest that conversion to carbon had occurred. SEM-EDX analysis confirmed that the black particles are made of light elements only. The biological nature of these black particles was also suggested by optical microscopy inspection: they come in spherical shape (Fig. 2) that can hardly result from a mineral matter. Further investigation is needed in order to determine the exact type of organism.

In another instance, a chromatic change was noted in a planetarium (Fig. 3 – painting no. 12P, Canova fraction) where the

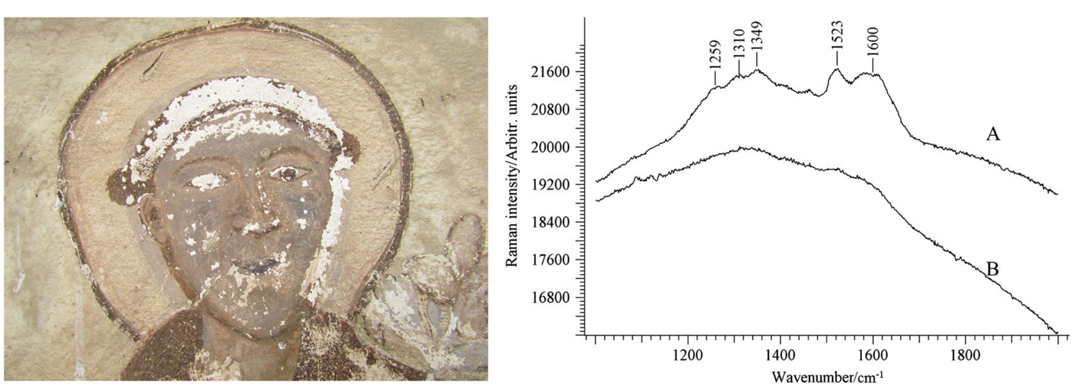

Figure 1. Painting no.44A, particular from Sant'Antonio face. Right: Raman spectra from a grey area, (a) spectrum from a black spherical particle at 0.3 mW laser power; (b) spectrum at full power. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs

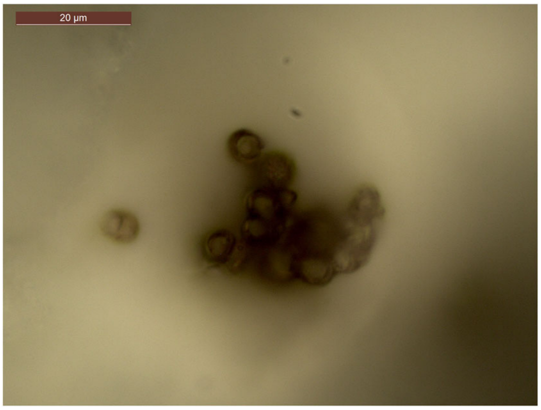

Figure 2. 100× image from a grey area on painting no.44A.

planets turned from the original red, obtained with red lead or minium – Pb_3O_4 – to the present black. Similar phenomena have been recently reviewed by Aze *et al.*[7] Again, it was not found the evidence of conversion of a lead pigment to galena. At low laser power (ca. 2 mW), the Raman spectrum shown in Fig. 3 was obtained from black particles: in this case, according to the main band present at 520 cm^{-1}, it can be concluded that plattnerite – PbO_2 – was the mineral phase formed as alteration of Pb_3O_4; this interpretation is in good agreement with the spectral features indicated by Burgio *et al.*,[8] and it was confirmed by SEM-EDX analysis, which yielded an atomic composition around 54/46% O/Pb from red particles but around 66/33% from black particles, in accordance with a PbO_2 stoichiometry. Though PbO_2 be relatively unstable and tend to change to Pb_3O_4, its stability is increased in alkaline environment (such as in fresco painting) and in conditions of high humidity.

Another chromatic alteration was noted on copper pigments. A painting with heavy discolouration (no. 3A, Pertusetto fraction) showed some green-blue areas; according to the iconography, light blue should have been the original hue. In fact, blue particles yielded the spectrum of azurite when analysed by Raman, whereas other green particles yielded the spectrum of a copper oxychloride, possibly paratacamite. The conversion of azurite to atacamite or other oxychlorides has been already reported[9–11] and can possibly be due to chlorine contribution from water percolating on the paintings.

Finally, in a single instance, on painting no. 66A (Villar fraction), it was evidence of alteration of smalt, a blue synthetic pigment used all along Renaissance. This feature will be discussed later.

Information concerning raw materials

Particularly notable was the information concerning the origin of raw materials. Being Ala di Stura, a mountain site with no easy access other than by pedestrian routes, the most reliable hypothesis is that artists provided themselves with materials obtained from local sources. On the other hand, the geographic area known as Lanzo valleys (Viù, Ala and Grande valleys) in which Ala di Stura has a nearly central position and is very rich in minerals: mines have been exploited since mediaeval times, mostly in the metallurgical industry, so that there was a potentially wide availability of pictorial materials. It is reported that iron and copper mines were in use at least since XIII century, whereas a cobalt mine was discovered in XVIII century.[12] Silver mines were present also, to which lead minerals were associated. This information allows thinking that a nearly complete palette was available for artists: iron oxides for warm hues, copper and cobalt pigments for cool hues, lead and calcium minerals for white and vegetal sources for black.

Results from Raman analysis on the artworks put into evidence a clear link among the pigments used by artists and sources of minerals available in the surrounding geographic area, allowing to confirm the hypothesis that these artists could supply themselves with local raw materials only, in particular for what concerns the older artworks. For the more recent artworks, pigments were obtained preferably, even if not exclusively, from local sources. In Table 1, a list of pigments identified in the oldest among artworks (<XIX century) is reported. The following comments are useful to support the hypothesis of local sources exploitation.

Table 1. List of pigments identified in the oldest artworks

Colour	Pigment identified	Raw material
Black	Carbon black	Vegetal carbon
Blue	Azurite	Azurite
	Ultramarine blue, natural	Lapis lazuli
	Smalt	Skutterudite
Green	Green earth	Celadonite
	Copper arsenates	Copper arsenates
Red	Iron oxide pigments	Hematite, red ochre
White	Lead white	Lead minerals
	Chalk	Calcite
Yellow	Iron oxide pigments	Goethite, yellow ochre
	Pyrite	Pyrite

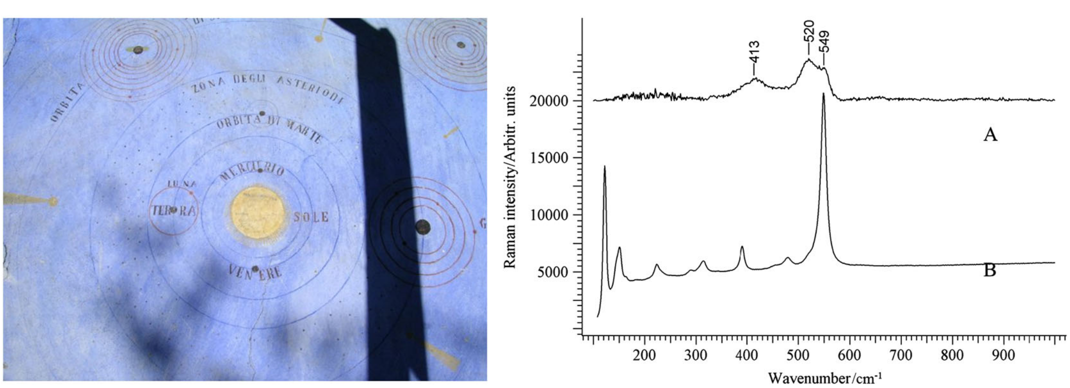

Figure 3. Planetarium no. 12P. Right: Raman spectra from a black area, (a) spectrum from a black particle; (b) spectrum from a red particle. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs

Plaster

A typical feature evidenced in all paintings is the occurrence of asbestos minerals, of which the Raman spectrum shown in Fig. 4 reports a typical example. This can be quite easily explained by considering the overall presence of serpentine rocks in the Lanzo valleys. According to the spectral features of the recorded spectra and making reference to the scientific literature,[13,14] it is possible to verify that these asbestos minerals are of the amphibole groups and in particular of the tremolite-actinolite series.

Blue pigments

Azurite, smalt and ultramarine blue were identified in blue areas. Azurite was identified by Raman analysis; the presence of the corresponding mineral is certified in different zones of the Lanzo valleys. Identification of ultramarine blue as *natural*, i.e. obtained from lapis lazuli, was supported by optical microscopy, as said before; its presence in the Lanzo valleys is not officially documented and it is indeed highly improbable, so that further bibliographical research is needed to verify the merceological aspects, i.e. to understand how lapis lazuli came to Ala di Stura from foreign sources. Smalt did not yield any Raman spectrum, due to poor scattering: it was, instead, identified by SEM-EDX, which evidenced the presence of Ni and As also, suggesting that skutterudite – $(Co,Ni)_{\times}As_{3-\times}$ – was the mineral source for it. According to written records, skutterudite has been excavated between 1753 and 1848 from Punta Corna mine, in the nearby valley of Viù; the ore extracted was exported mainly to Germany to be used in the glass industry. Another cobalt mine was present at Balme, near Ala di Stura.[12]

Green pigments

Green earth and copper arsenates were the green pigments identified. Green earth, identified by Raman analysis, was most probably of the celadonite variety as suggested by Ospitali *et al.*[15] according to peaks occurring at 271, 391 and 553 cm^{-1} and in the region of hydroxyl stretching (Fig. 5); in fact, celadonite is present at Balangero and Monastero di Chiaves, two sites located at the beginning of Lanzo valleys. Copper arsenates were identified by Raman analysis in reason of bands in the range 850–865 cm^{-1} (Fig. 6), which can be assigned to AsO_4^- symmetric and asymmetric stretching; this attribution was confirmed by SEM-EDX, which evidenced the presence of Cu and As. It is not easy to determine unequivocally the compound/compounds present because different copper arsenates exist. Among them, olivenite $[Cu_2(AsO_4)(OH)]$, cornwallite $[Cu_5(AsO_4)_2(OH)_4]$, mixite $[Cu_6Bi(AsO_4)_3(OH)_6{\cdot}3H_2O]$ and conichalcite $[CaCu(AsO_4)(OH)]$ are known to occur as minerals in the Lanzo valleys, whereas clinoclase $[Cu_3(AsO_4)(OH)_3]$, lammerite $[Cu_3(AsO_4)_2]$ or cornubite $[Cu_5(AsO_4)_2(OH)_4]$ are not. According to the spectral features described by Frost *et al.*,[16] the most probable phase is olivenite, but cornwallite can be present as well. On the other hand, semi-quantitative analysis with SEM-EDX gave a 1 : 1 ratio among copper and arsenic, which is more consistent with conichalcite. Indeed, because the spectral information obtained from green areas do not match exactly a single standard copper arsenate, it is possible to think that either a mixture of arsenates is present in these samples or the minerals were treated to improve their quality from the chromatic point of view, thus determining a phase change. The use of copper arsenates to paint green areas is nevertheless surprising because they have been rarely identified in the past. Aliatis *et al.*[17] suggested the presence of copper arsenates in the remains of a green pigment found in Pompei excavations; in that case, although copper arsenates seemed not to be the main colouring phase. Baraldi *et al.*[18] identified agardite, a complex copper arsenate containing lanthanide ions also, in blue painted areas in fragments of fresco painting from San Francesco Basilica in Assisi. Finally, Zeng *et al.*[19] identified a copper arsenate on a XX century Chinese shrine, tentatively marked as cornwallite.

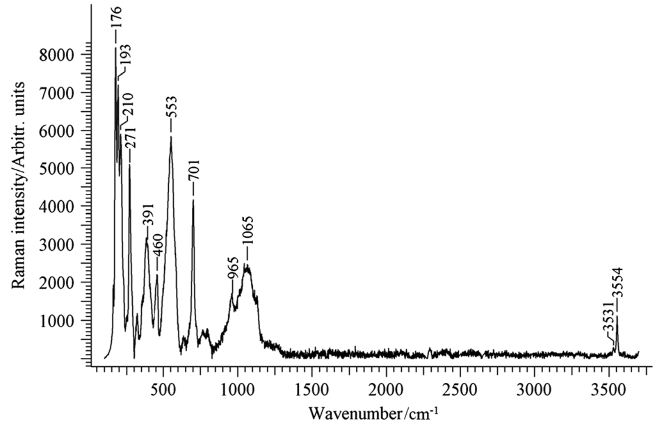

Figure 5. Raman spectrum of green earth of the celadonite variety from a green area.

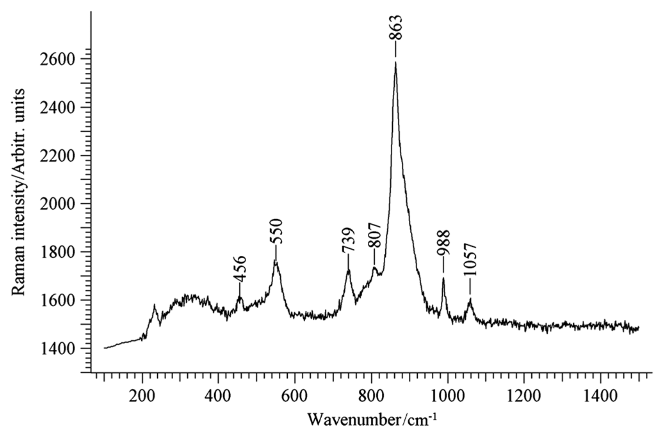

Figure 6. Raman spectrum of a copper arsenate from a green area.

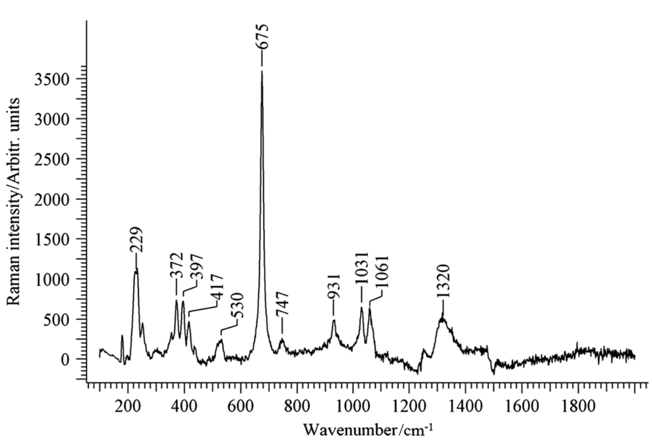

Figure 4. Raman spectrum of an asbestos mineral of the amphibole group.

Red pigments

The presence of iron oxide pigments (hematite and red ochres) in the artworks is easily determined by Raman spectroscopy, as is red lead. Many sources of iron minerals are certified in the Lanzo valleys and their exploitation is known since mediaeval times, being an important resource for the local economy.

White pigments

Calcite was identified in the more ancient frescoes, whereas white lead was identified in the more recent ones. The presence of calcareous minerals is ubiquitous; for what concerns lead minerals, in the Lanzo valleys sources of cerussite and galena are present, sometimes associated with silver.

Yellow pigments

Yellow ochre and goethite were identified in the artworks as only yellow pigments, with the exception of pyrite that will be discussed later. As for red pigments, the availability of yellow iron oxides is guaranteed by the high number of iron mines in the valleys.[12]

Accessory phases

In order to have further information on the origin of the pictorial materials used in Ala di Stura artworks, identification of accessory mineral phases other than the colouring phase was systematically performed in all samples of paint analysed. Apart from the asbestos minerals previously cited, the following minerals were identified: albite, anatase, baryte, diopside, epidote, magnetite, quartz, rutile and tourmaline. All of them are minerals present in the Lanzo valleys.

Interesting is also the relationship among diagnostic information and historical information regarding the exploitation of mineral sources inside the area. Identification of some pigments on paintings bearing a certain date can spread light on the history of the use of minerals as sources for pigments, in parallel with their use for industrial or military reasons. This is typically the case of cobalt minerals whose exploitation from local sources is reported, on bibliographic basis, from the first half of XVIII century, but whose presence has been identified by SEM-EDX as raw materials for smalt on some XVI–XVII century paintings among Ala di Stura artworks: in this case, most probably the historical information must be updated according to analysis results. It is interesting to compare the elemental composition of smalt particles, as determined with SEM-EDX, in three different paintings datable among XVI and XVII century: it can be seen from Table 2 that compositions, expressed as atomic percentages, are similar in terms of accompanying elements (e.g. Fe, Ni and As), suggesting the hypothesis of a common source, possibly the already cited Punta Corna mine.

Table 2. Semi-quantitative SEM-EDX analysis on smalt particles from different paintings

Element	5A*	23A*	66A*
Al	0.7	0.8	0.9
Si	25.0	27.8	31.9
K	4.3	5.8	1.2
Ca	0.9	1.7	1.4
Fe	1.1	1.0	1.3
Co	1.0	1.0	1.1
Ni	0.4	0.2	0.3
As	0.9	0.5	1.0

* atomic percentages

Finally, in the course of this diagnostic study, the role of Giovanni Oldrado Perini di Novalesa, an almost unknown Renaissance painter, has been put into evidence. His paintings, dating from the second half of XVI century, are among the oldest and also the most valuable in the whole of Ala di Stura artwork heritage. Perini was a Benedictine monk coming from Novalesa Abbey (Val di Susa, Piedmont) who used to travel in the 1570s and 1580s in Canavese and Lanzo valleys. His artistic activity in some sites such as Ala di Stura, Ceres or Corio Canavese is witnessed by historical documents that report rewards for his jobs.[20] In Ala di Stura, three residual paintings of this artist still survive, coded no. 24A (Prussello fraction), 46A (Pian del Tetto fraction) and 66A (Villar fraction). On the basis of analysis carried out on these paintings, the palette used by Perini, listed in Table 3, seems to be rather poor for what concerns the value of the pictorial materials used, because mostly iron oxide pigments are present. More interesting is the fact that all pigments, again, are based on mineral sources available in the valleys. Moreover, if we look on the Virgin's robe in painting no. 66A (Fig. 7), it appears of grey hue, a feature that is not consistent with the traditional iconography. Indeed, SEM-EDX analysis on a sample of the grey area allowed to identify the residual presence of smalt particles. It is known that smalt is subjected to discoloration due to migration of K^+ and Co^{2+} ions;[21] but in this case, the most probable hypothesis is that of a poor paint preparation that caused almost complete detachment of the pigment from the painting. This alteration, in fact, was verified only in painting no. 66A; it is difficult, therefore, to think that conditions suitable to promote discolouration had occurred in this place and not in other places Raman analysis allowed to elucidate details on the pictorial technique of this artist. Of particular relevance was the use of pyrite (Raman spectrum in Fig. 7), a mineral available in the area, mixed with smalt, possibly to give a more shining appearance to the Virgin's robe or at least to reproduce a chromatic aspect similar to lapis lazuli, being pyrite naturally present as an accessory mineral phase of the precious stone. Pyrite has already been identified by Bersani *et al.*[22] in a blue painted area made of ultramarine blue on the 'Madonna col Bambino e S. Giovannino' by Botticelli, but in that case it was not possible to determine whether the artist intentionally added pyrite to lapis lazuli.

Dating artworks

For what concerns dating of artworks, in some instances a written date was found on them, but in many other instances dating was based on stylistic considerations only. For this reason, we looked for pigments acting as time markers, i.e. materials whose introduction date in painting art was well established; finding one of such pigments on an artwork could help in defining a *post quem* date for its creation. This is particularly effective for synthetic

Table 3. The palette of Giovanni Oldrado Perini di Novalesa

Colour	Pigment identified
Black	Carbon black
Blue	Smalt
Green	Green earth
Red	Iron oxide pigments
White	Chalk
Yellow	Iron oxide pigments
	Pyrite

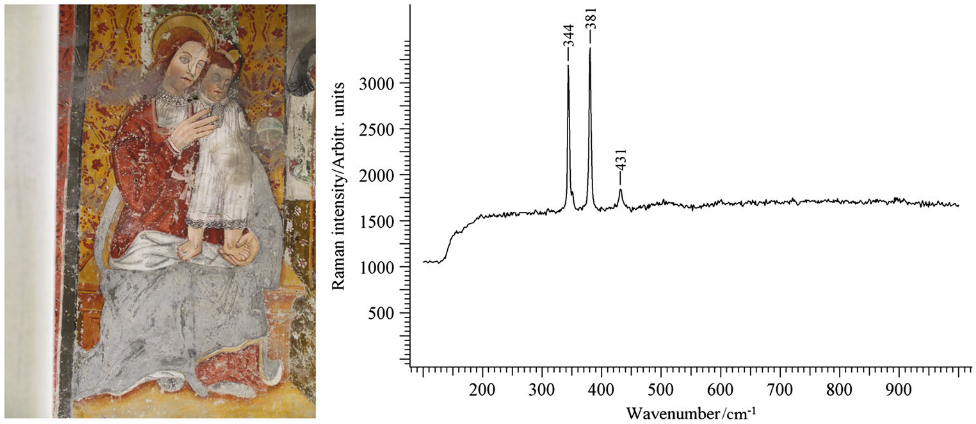

Figure 7. Painting no.66A, detail with the Virgin and Child; grey cloak is evident. Right: Raman spectrum of pyrite. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs

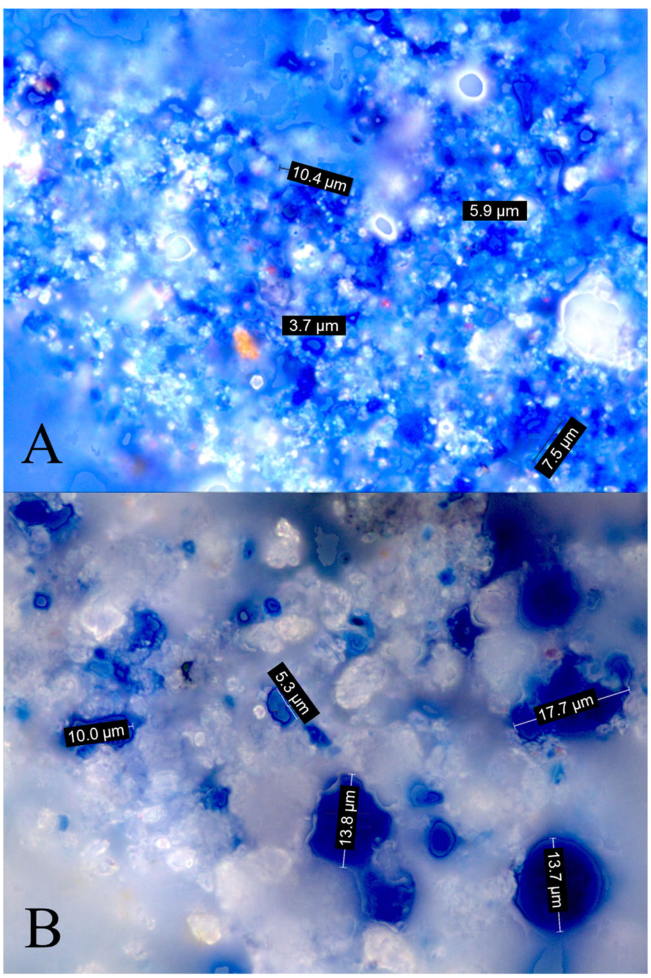

Figure 8. Ultramarine blue grains, 100× images from (a) meridian no. 75 M and (b) painting no. 63A. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs

pigments produced from 1700 afterwards, for whom a wide bibliography exists.[23]

A pigment occurring in several instances in Ala di Stura artworks is ultramarine blue, according to the results of Raman analysis on blue painted areas; this is particularly true for meridians, while for paintings it was found only in the newer ones. The occurrence of ultramarine blue is useful in reason of the temporal difference among the natural version, made from lapis lazuli rock and used since 5000 years ago, and the artificial version firstly synthesised in 1828, as is well known. Indeed, natural and artificial versions are not distinguishable among themselves on the basis of the Raman spectra; visual inspection through optical microscopy, on the contrary, could help in discriminating them because the natural version, obtained by grinding a rock, is composed by larger irregularly shaped particles, whereas the artificial version is made of smaller regularly shaped particles. A comparison is shown in Fig. 8 where it can be seen: (1) a sample of synthetic ultramarine blue from meridian no.75 M, with particles averaging 5 μm in diameter; and (2) a sample of lapis lazuli from painting no. 63A, with particles in the range 10–20 μm. On this basis, in all but one Ala di Stura artworks, it was found evidence of synthetic ultramarine, so that all the corresponding artworks can be safely dated after 1828. In one case only, that of painting no. 63A (Villar fraction), blue particles of diameter larger than 10 μm were found, so that this could be the only artwork containing lapis lazuli. It could be interesting to verify where the pigment came from by applying other analytical techniques to determine its provenance.[24]

Other pigments identified in Ala di Stura artworks and acting as time markers were the artificial arsenic-containing green pigments *Scheele's green* and *Emerald green*, respectively synthesised in 1775 and in 1808. Again, these pigments, identified by their characteristic Raman spectra, give an accurate *post quem* date for the paintings containing them.

Conclusions

Raman analysis performed on the samples withdrawn from several artworks in Ala di Stura allowed to yield a wide amount of information on the conservative, historical and artistic aspects of these artworks. This information will be used in order to address the conservation issues and to have a better knowledge of the meaning and the techniques used in painting.

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