

Degradation of Emerald Green: Scientific Studies on Multi-polychrome Vairocana Statue in Dazu Rock Carvings, Chongqing, China

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Abstract

The spontaneous degradation of pigments in painting may occur depending on environment, especially the surrounding condition of high humidity and soluble salts. Even some of these are well studied, more investigations are still in need for heritage science. Paint cross sections from Vairocana Statue in Dazu Rock Carvings, one of World Cultural Heritage, Chongqing, China are studied by optical microscopy (OM), Raman spectroscopy (Raman) and mapping, and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDS). Ultramarine blue, emerald green, synthetic atacamite, vermilion, red lead, gold foil, orpiment, cerussite, gypsum and barite are identified as pigments. Moreover, lavendulan ($\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$) and mimetite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$) are degradation products of emerald green ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 3\text{Cu}(\text{AsO}_2)_2$) and cerussite (PbCO_3) originally used as green pigment with mixture. These secondary products is formed via multistep progresses as degradation of emerald green and cerussite, oxidation of arsenite ($(\text{AsO}_2)^-$), migration of arsenate ($(\text{AsO}_4)^{3-}$) and precipitation reaction of these ions with other necessary ions from environmental conditions. Based on the pigment and paint layer stratigraphy analysis, the paintings of the statue have been executed at least four times and the most recent may be after 1850s. The formation of lavendulan give rise to a highlight for identification of green copper-arsenic containing pigments and characterization of degradation in complex conditions.

Introduction

Degradation phenomena occur in the paintings where original pigments, binding media, ground layer and substrate to undergo chemical and physical transformations, leading to discolouration or deterioration of materials. These processes can be initiated by internal factors, for example the characteristics of pigments with organic binders and other materials, or by external factors, which suffer from environmental conditions (relative humidity, illumination, temperature, etc), biological activity, pollution or human interventions, or several of these together [1]. Degradation of pigments can be visually perceived as color changes or confirmed as structural modifications by employing modern analytical or micro-analytical methods.

Studies on degradation processes and products of pigments inside museum on oil paintings, manuscripts and in an outdoor environment on polychrome statue and wall paintings are well known and documented. Azurite ($2\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$) and malachite ($\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$), as the best representatives of basic copper salts (carbonates, chlorides, sulphates, etc.), are widely used as mineral blue and green pigments. In the case of artifacts, the published data indicates the transformation of azurite and malachite into green basic Cu chlorides in the presence of chloride and humidity [2]. Arsenic-based pigments such as orpiment (As_2S_3) and realgar (As_4S_4) are highly appreciated in China for yellow and red to red-orange tones. Arsenic sulfide pigments are bound to shift color exposed to visible light and realgar undergoes photo-induced polymorphism and becomes friable, assuming hues from bright yellow pararealgar (As_4S_4) to colorless arsenolite (As_2O_3) whereas the photo-oxidation of orpiment results in arsenolite [3]. Lead pigments e.g. lead white ($2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$), red lead (Pb_3O_4) are employed owing to

bright colors and high covering power in paintings. Lead pigments turn black caused by reaction with sulphur-containing compounds to black galena (PbS) and oxidation to the black-brown plattnerite (PbO₂) [1]. Vermillion (HgS) is extensively used as bright red pigment. It darkens attributed to the formation of a black compound, metacinnabar (β-HgS) when exposed to light and HgCl₂ when Cl⁻ ions present in the pigments [2].

A popular man-made brilliant green pigment, Emerald green (Cu(C₂H₃O₂)₂·3Cu(AsO₂)₂), containing copper and arsenic is found to be unstable in paints. Emerald green darkens as it mixed with sulphur-containing compounds from the atmosphere to form brown copper sulfides (CuS) [3]. Emerald green degrades in oil paintings rich with a relatively high concentration of monoacids, diacids and resin acids, forming copper soaps (4Cu(FA)₂) (FA = fatty acids) and arsenic trioxide (As₂O₃), leading to transparent discolored brown layers [4]. Emerald green is also found to transform to mineral lammerite (Cu₃(AsO₄)₂) in wall paintings as a result of the migration of arsenic [5]. Recently, rare lead arsenate mineral, mimetite (Pb₅(AsO₄)₃Cl), is shown to be degradation product of multistep alteration pathway of pigments orpiment and realgar and arsenate ions ((AsO₄)³⁻) to precipitate with Pb²⁺ ions [6].

Naturally, taking physical and chemical conditions of their usage and storage into account, pigments in wall paintings and polychrome statues are much more subjected to the environment, even in complex conditions including high humidity or dissolved salts. Even some of these are well studied above, more tracking and new investigations are still needed and crucial for the conservation field.

In 2016, China's National Cultural Heritage Administration launched a large-scale perseveration demonstration projects for the Buddhism Grottoes in Sichuan Province and Chongqing Municipality. At that time, a subproject aiming to conserve and restore the Niche of Sakyamuni Entering Nirvana Statue in Great Buddha Bend (Dafowan, 大佛湾) and Polychrome Statues in Little Buddha Bend (Xiaofowan, 小佛湾) at Dazu Rock Carvings (大足石刻) was undertaken by the Chinese Academy of Cultural Heritage. Located outdoors in a long time, the statues have been inevitably suffering from surface weathering, water seepage, rock instabilities, biological erosion, salt corrosion, etc, so the scientific investigation and Conservation is becoming urgent. The first step is to investigate the characteristics of the paintings on caved sandstone surface for determining the appropriate intervention treatment. Therefore, the polychrome statue Vairocana Statue in Little Buddha Bend at Dazu Rock Carvings of Chongqing municipality was chosen as a demonstration example.

In this study, a coupling of Raman spectrum and mapping, OM, and SEM-EDS have been applied to identify the composition of original pigments and signs of their degradation in cross sections of color layers from paintings of polychrome statue Vairocana Statue. The information obtained can accelerate a better understanding of the transformation processes which affect the history and stability of paints. Material identification of layer stratigraphy can confirm the date of paintings executed.

Materials And Methods

Materials

Outstanding as the pinnacle of Chinese cave temple art from the 9th to 13th centuries, Dazu Rock Carvings were listed as World Cultural Heritage by UNESCO in 1999. The sites are located in Dazu District, Chongqing, China, comprised of the cliffside carvings at Baodingshan, Beishan, Nanshan, Shizhuanshan and Shimenshan. Dazu Rock Carvings are remarkable for their aesthetic quality, their rich diversity of subject matter, both secular and religious, and the light that they shed on everyday life in China during this period. They provide outstanding evidence of the harmonious synthesis of Buddhism, Taoism and Confucianism [1].

The culmination of carvings are found on Mount Baoding, consisting of two groups from the late 12th to the mid 13th century, namely, Great Buddha Bend and Little Buddha Bend.

The Vairocana Buddha Statue (measuring 1.92×1.57 m) is the Lord Buddha of whole Little Buddha Bend statues. The paintings have been re-painted several times observed by naked eyes and seriously damaged. For examples, they are seen as the numerous colour losses, cracking and crumbling of the pictorial layer. Some paintings become powder-like substances. Dust is deposited on the paint surface, and the cracked areas easily gather the dust from the environment. Sixteen micro samples including blue, green, red, gilding, black and white color are collected from the painting of this statue (Fig. 1).

Methods

Sixteen samples, including different paint layer and ground layer, are prepared and studied on the cross section (CS). For cross section samples, the minute pigments are embedded in epoxy resin (Buehler Epo Thin) and polished with dry abrasive papers down to $0.5 \mu\text{m}$ to obtain sufficiently polished surface. Each layers of these samples are analyzed by Optical microscope (OM), micro-Raman spectroscopy (Raman) and scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS).

The samples are observed using a Lecia 4000M optical microscope.

A Horiba Jobin Yvon Xplora spectrometer coupled with $100\times$ objective of an Olympus BX-41 microscope is employed for identification of pigments in each painting layers. The 532 nm green and 785 nm red laser is used and the spectrum is recorded with a resolution of 2 cm^{-1} . The spectra of pigment particles are representative and chosen from at least three different points. Moreover, the laser power for identifying green pigments was reduced using 1% filter, to avoid the thermal photodecomposition. The exposure time was 10 seconds with 20 accumulation.

The cross section samples are coated with carbon and studied under a TESCAN VEGA3 scanning electron microscope, equipped with Bruker XFlash 610M energy dispersive X-ray at an accelerating voltage of 20 KV.

Results And Discussion

Paint layers

The structure and materials of the Vairocana Statue are very complex, including sandstone substrate, gilding and paintings. The components of non-degraded sandstones of the rock carving are feldspar, quartz, plagioclase, calcite, and a small amount of clay [1]. OM and SEM results of cross sections show the samples are built up in multilayers including CS 1, CS 5, CS 10, CS 11, CS 13 and CS 16, and visible layers are numbered 1 ~ 7 or 8 from the surface to inner in Fig. 2. Table 1 summarizes multi-paint stratigraphy and layer composition of these samples examined by Raman and EDS. The other ten samples illustrate that delamination phenomena are not visible i.e. one paint layer close to ground layer. Blue pigment CS 2, CS3 and CS4 show two distinct layers. The top layer is composed of Ultramarine blue and the bottom layer i.e. ground layer composed of gypsum (by Raman), calcite (by Raman), quartz (by Raman) and clay (by SEM-EDS) as the presence of elements e.g. Na, Mg, Al, Si, S, Ca and Fe consistent with XRD analysis results [1]. Green layer of CS 6, CS 7 and CS 8 is mixture of lavendulan, mimetite, cerussite, barite, whewellite and gypsum, and the ground layer consist of gypsum, calcite, quartz and clay. Red layer of CS 9 and CS12 is composed of vermilion, and black layer of CS 15 contains carbon. Gold foil layer (~1 μm) of CS 14 is consist of Au content 96.4 wt% and Ag 2.8 wt%. The gold plastic paint used to bond gold foil are defined as the base layer close to the sandstone substrate. The plastic paint is made of Chinese lacquer and addition of tung oil by use of FTIR and GC/MS [1] and divided into three layers (similar to layer 2, 3 and 4 in Fig. 2e) e.g. red lacquer layer mixed with vermilion to high gold foil gloss, black lacquer layer, and gray lacquer layer mixed with quartz and clay to smooth the adhered surface of sandstone.

Table 1 Layer stratigraphy and components of cross sections

Code	Layer	Colour	Identified components	Code	Layer	Colour	Identified components
CS1 Fig.2a	1	Blue	Ultramarine Blue	CS2 Fig.2b	1	Green	Emerald green, lavendulan, mimetite, cerussite, gypsum, barite, whewellite
	2	Gray	Gypsum, calcite, quartz and clay		2	Green	Lavendulan, mimetite, cerussite, gypsum, barite, whewellite
	3	Blue	Ultramarine Blue		3	Gray	Gypsum, calcite, quartz and clay
	4	Gray	Gypsum, calcite, quartz and clay		4	Blue	Ultramarine Blue
	5	Blue	Ultramarine Blue		5	Gray	Gypsum, calcite, quartz and clay
	6	Gray	Gypsum, calcite, quartz and clay		6	Yellow	Orpiment
	7	Red	Vermilion		7	Gray	Sandstone substrate
	8	Gray	Sandstone substrate				
CS5 Fig.2c	1	Red	Vermilion	CS11 Fig.2d	1	Red	Vermilion
	2	Orange	Red lead		2	Orange	Red lead
	3	Gray	Gypsum, calcite, quartz and clay		3	Gray	Quartz and clay
	4	Black	Carbon, calcite, lead white		4	Green	Lavendulan
	5	Gray	Gypsum, calcite, lead white and clay		5	Gray	Quartz and clay
	6	Orange	Red lead, Vermilion		6	Orange	Red lead
	7	Gray	Sandstone substrate		7	Gray	Sandstone substrate
CS13 Fig.2e	1	Gold	Gold foil (Au 99.3 wt%, Ag 0.7 wt%)	CS16 Fig.2f	1	White	Cerussite
	2	Red	Chinese lacquer addition of tung oil, vermilion		2	Gray	Quartz and clay
	3	Black	Chinese lacquer addition of tung oil		3	Orange	Red lead
	4	Gray	Chinese lacquer addition of tung oil, quartz and clay		4	Gray	Quartz and clay
	5	Gray	Quartz and clay		5	White	Cerussite, gypsum, calcite, quartz and clay
	6	Yellow	Orpiment		6	Green	Malachite, Atacamite
	7	Gray	Quartz and clay		7	Gray	Sandstone substrate
	8	Red	Vermilion, red lead				

Green copper arsenite pigments

Raman analysis on cross sections demonstrates that lavendulan and emerald green in the samples investigated, and no other copper-arsenic containing pigments are detected. Lavendulan is the main constituent of green pigment (e.g. Figure 3b) mixed with mimetite, cerussite, gypsum, barite and whewellite (e.g. Figure 3c and Fig. 3d) on CS 5 ~ 8. However, emerald green is only in the bottom of the green layer (marked 2 in Fig. 2b) of CS 5 (Fig. 3a).

Further observations with OM and SEM-BSE for CS 5 show the top of the green layer (layer 1 in Fig. 4a) losing the green coloration comparing with the bottom (layer 2 in Fig. 4) caused by the absence of emerald green. The lavendulan particles show single plates radiating from center to edges with a diameter of $\sim 10 \mu\text{m}$ and spherulites formed by the plates overlapping or intersecting at the center in Fig. 4b and c. Although lavendulan particles occur with color of pale blue (Fig. 4b), their general crystal habit and structure is consistent with that of emerald green [13]. Nevertheless, the natural lavendulan forms bright blue crusts, spherules and thin rectangular platelets which are flexible and have a low Mohs hardness (2.5) and excellent cleavage parallel to the platy face [14]. These results suggest that lavendulan is a degradation product of emerald green. The elemental maps of the green layer corresponding to BSE image (Fig. 4d) show the distribution of copper, arsenic, sodium, calcium and chlorine (Fig. 4e-i). The arsenic is not confined to the green particles, and migrates throughout the whole green layer, while the copper distribution is limited to particles. This is similar to observation of the migration of arsenic from the arsenic-containing pigments to paint layers [15]. Furthermore, the absence of arsenic in the blue, gold, red and black samples and paints excludes the possibility of arsenic introduced from the surrounding environment to the green paint. An explanation for the presence of arsenic in the green layer could be deriving from degraded emerald green. The distributions of Na, Ca and Cl in green layer also suggest these elements introduced from the surrounding environment and then react with Cu and As to form lavendulan.

Distributions of crystalline phases of a sub area in green layer (2 in Fig. 2b) of CS 5 obtained with Raman mapping show further details in Fig. 5. In this subarea, emerald green is confirmed as green pigment and surround by cerussite as shown in Fig. 5a and Fig. 5b. Next to emerald green (point 1), distributions of lavendulan (point 2, 3 and 4) are quite different (see Fig. 5c). Mimetite is found in the vicinity of green particles and shows a higher abundance in the areas around lavendulan particles (especially point 3) than that around emerald green (see Fig. 5d). These results suggest arsenic derived from the degraded emerald green particles must have reacted with cerussite to form mimetite as secondary products.

Green copper hydroxychloride pigments

Regarding the green layer of CS 16, layer structure and composition are investigated by Raman, OM and SEM-EDS.

Raman analysis shows the existence of atacamite and malachite in the green layer (layer 6 in Fig. 2f) of CS 16 (Fig. 6). Figure 7a, b and c mainly show that numerous atacamite particles appear as aggregates or masses, while malachite particles sporadically occur in the layer. The synthetic atacamite particles are found to be spherical with dark spots in the centre under the PLM [16]. Figure 7b, c, d and g reveal nearly spherical particles, typical for synthetic atacamite. Malachite could be obtained as a by-product of preparation of synthetic atacamite. Artificial copper trihydroxychlorides could be the most popular green pigments for wall painting and architecture from North Dynasty (386–581 CE) until late Qing Dynasty (1840–1911 CE) [17]. In addition, the element maps of chlorine associated with copper (Fig. 7e-f and Fig. 7h-i) show delamination phenomena in the green layer is invisible, suggesting the green layer was painted only one time other than repainted using the two kinds of green pigments.

Discussion on dating

Emerald green is a brilliant green pigment first synthesized by Willem Sattler in 1814. Emerald green particles exist in a great variety of crystalline assemblages that are organized as agglomerates of crystal platelets in the form of rosettes or spherulites [13]. It was widely used in China as watercolor in pith paper works and in scroll paintings from the 1850s onwards [14]. Ultramarine blue show rounded anisotropic particles of homogeneous sizes ($\approx 2 \mu\text{m}$), suggesting the artificial origin of the lapis lazuli [15] are used in the out layer of the painted statues. Artificial ultramarine blue was invented by Guimet in 1828 and its commercial production evolved soon after 1830 [16]. Then ultramarine blue was introduced from Europe into China in late Qing Dynasty (1840 ~ 1912 CE), and the importation lasted until 1927 when Chinese chemists Dai A and Ling Z synthesized this pigment [17].

The statues in the Little Buddha Bend at Dazu Rock Carving was excavated during the Southern Song Dynasty (1127 ~ 1279 CE) [18]. Religious paintings in China usually undergo heavy repairs and even re-painting in different period. As the layer stratigraphy shown (Fig. 2) shown, for more than 800 years so far, the Vairocana Buddha statue has been painted at least four times. Concerning these documents above, the most recent painting of the statue may be executed after late 1850s, based on the date of the wide use of emerald green.

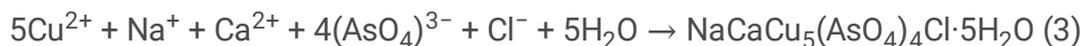
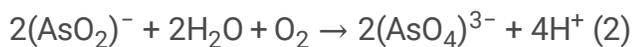
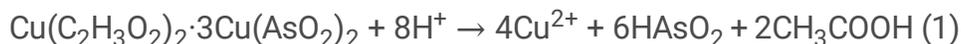
Because the date of the invention and wide use in China of emerald green and ultramarine blue were nearing, they appeared co-localized in Chinese paintings. In addition, consistent with the recent literature on this topic [16,17,18], the rare nature of mimetite minerals strongly suggests that they are secondary products. Once more this information suggests emerald green was used as original pigment other than lavendulan (secondary products).

Degradation progress of emerald green

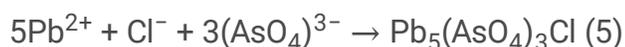
The Vairocana Buddha statue is located in the Holy Longevity Sites, where the air circulation is poor because of the semi-closed building structure. Relative humidity in the Dazu Rock Carvings is very high and can reach above 85% from July to September, even oversaturated to form condensation water with pH scale at 6 on the surface of statues [19]. The stone statues carving contain more soluble salts, specifically SO_4^{2-} , Cl^- , Na^+ and Ca^{2+} [20]. When exposed to such conditions, degradation phenomena of pigments can occur, namely transformation from emerald green to lavendulan in the paint surface. It can be explained as follows:

The degradation of emerald green pigment occur under acidic conditions provided by the environment [15]. Emerald green ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$) releases acetic acid (CH_3COOH) together with arsenite (HAsO_2) and copper ions (Cu^{2+}) in the slightly acidic environment (Eq. 1). In the next step, the arsenite ions ($(\text{AsO}_2)^-$) are oxidised to arsenate ions ($(\text{AsO}_4)^{3-}$). The acidic environment and the acetic acid produced in the Eq.1 decrease the pH of the environment so that, in exposure to air, the arsenite ions are slowly transformed to arsenate ions (Eq. 2) [14]. The last step involves the reaction of $(\text{AsO}_4)^{3-}$ and Cu^{2+} , Na^+ , Ca^{2+} and Cl^- which triggers the formation

of lavendulan ($\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$) (Eq. 3). The formation of lavendulan needs acidity [], in dependence on pH of environment with condensation water and acid rain.



Cerussite is identified as extender minerals added to the paint, which enwraps the emerald green by using Raman mapping. The dissolution of cerussite (PbCO_3) occur in the aqueous phase which can be enhanced in acidic solution and releases the Pb^{2+} ions. The acidic groups from environment are sufficient to promote the dissolution process [], with consume of free protons and release of CO_2 (Eq. 4) [16]. The solvated arsenate ions ($(\text{AsO}_4)^{3-}$) that are supplied from the hydrolysis of emerald green migrating toward Pb^{2+} ions react with Cl^- ions to produce the precipitation of mimetite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$) (Eq. 5).



Simultaneously, calcium oxalate, e.g. whewellite $\text{CaC}_2\text{O}_4\cdot \text{H}_2\text{O}$, is also founded together with lavendulan by Raman (Fig. 3d). Oxalate salts are formed by calcium ions reaction with oxalate ions over a wide pH range, and commonly occur in art objects. The source of oxalate ions can be described as metabolic products of microorganisms living on the surface of paintings. It is especially relevant for objects in outdoor conditions, e.g. sculptures and wall paintings []. More likely, the statue surface of the Little Buddha Bend is proved to grow mould []. Oxalate ions are also suspected to release during degradation of emerald green in Eq. 1.

Furthermore, this discovery of lavendulan in Chinese painting is seldom reported. It is detected in the Cave 11 of Yungang Grottoe (洞窟), Shanxi Province and colored drawing on timber structure of Kumbum Monaster (塔), Qinghai Province []. We also find lavendulan on paintings of Maidservant figures in the Saint Mother's Hall of Jinci Temple (庙), Shanxi Province. In this study, emerald green has low permanence in the environment of high moisture and soluble salt. This work may help the scholars draw attention to the existence of degradation phase when investigating pigments in complex environment system, e.g. emerald green in damp and salt containing conditions. It also help scholars rethink about rare minerals as original pigments or degradation products. Because of wide usage of emerald green in China, rare copper-arsenic containing minerals could have a high propensity to be identified as degradation products in the patings after the late Qing Dynasty. Synthetic pigments is crucial for interpreting the historical context of cultural objects, especially for the dating.

Conclusion

In the conservation field of heritage science, study on degradation or corrosion of paint materials e.g. pigments plays a vital role in solving key questions of conservation, restoration and storage. In this study, secondary arsenate minerals, namely lavendulan and mimetite, are formed due to the degradation of emerald green and cerussite in the slightly acid and highly humid conditions. This process appears to be: formation of arsenate and copper ions as a result of degradation of emerald; migration of these ions including partially arsenate ions towards the surrounding area where dissolution of Pb^{2+} ions from cerussite and Cl^- ions from environment to product precipitation of mimetite; copper ions remaining in their original place together with arsenate ions and Na^+ , Ca^{2+} , Cl^- to form lavendulan.

The formation of lavendulan gives rise to a highlight for green copper-arsenic containing pigment identification as once generally considered to be emerald green and in turn remind the scholars rethink about the rare minerals discovered in the painting as pigments or degradation products.

Obtained from identification of painting layer stratigraphy, the information is crucial for understanding the context of cultural heritage objects regarding relative date of creation, painting technique and artists' savoir faire. The analysis of paint cross section from Vairocana Statue in Dazu Rock Carvings, Chongqing, China reveals an example of discrimination the paint dating via material research results. Ultramarine blue, emerald green, synthetic atacamite, vermilion, red lead, gold foil, orpiment, cerussite, gypsum and barite are identified as pigments. Based on the pigment analysis and historical documents, the paintings of the statue have been executed at least four times and the most recent may be after 1850s.

It also demonstrates that Raman spectroscopy mapping and element mapping corresponding with the layer stratigraphy on paint cross section have reliable performance for identification of the components and discrimination between products resulting from degradation processes, especially in the characterization of pigments in complex conditions.

Abbreviations

UNESCO: United Nations Educational, Scientific and Cultural Organization

Raman: micro-Raman spectroscopy

OM: optical microscopy

SEM-EDS: scanning electron microscopy with energy dispersive X-ray analysis

CS: cross section

Declarations

Authors' contributions

QM provided support and guidance for this study. ZL performed the analysis. ZL, LW and HC carried out literature. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials

The datasets used during this study are available from the corresponding author on reasonable request.

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Figures



Figure 1

Vairocana Buddha in the Little Buddha Bend at Dazu Rock Carvings. The sample location for (1 ~ 4) blue, (5 ~ 8) green, (9 ~ 12) red, (13 ~ 14) gold, (15) black, and (16) white pigments on the painting.

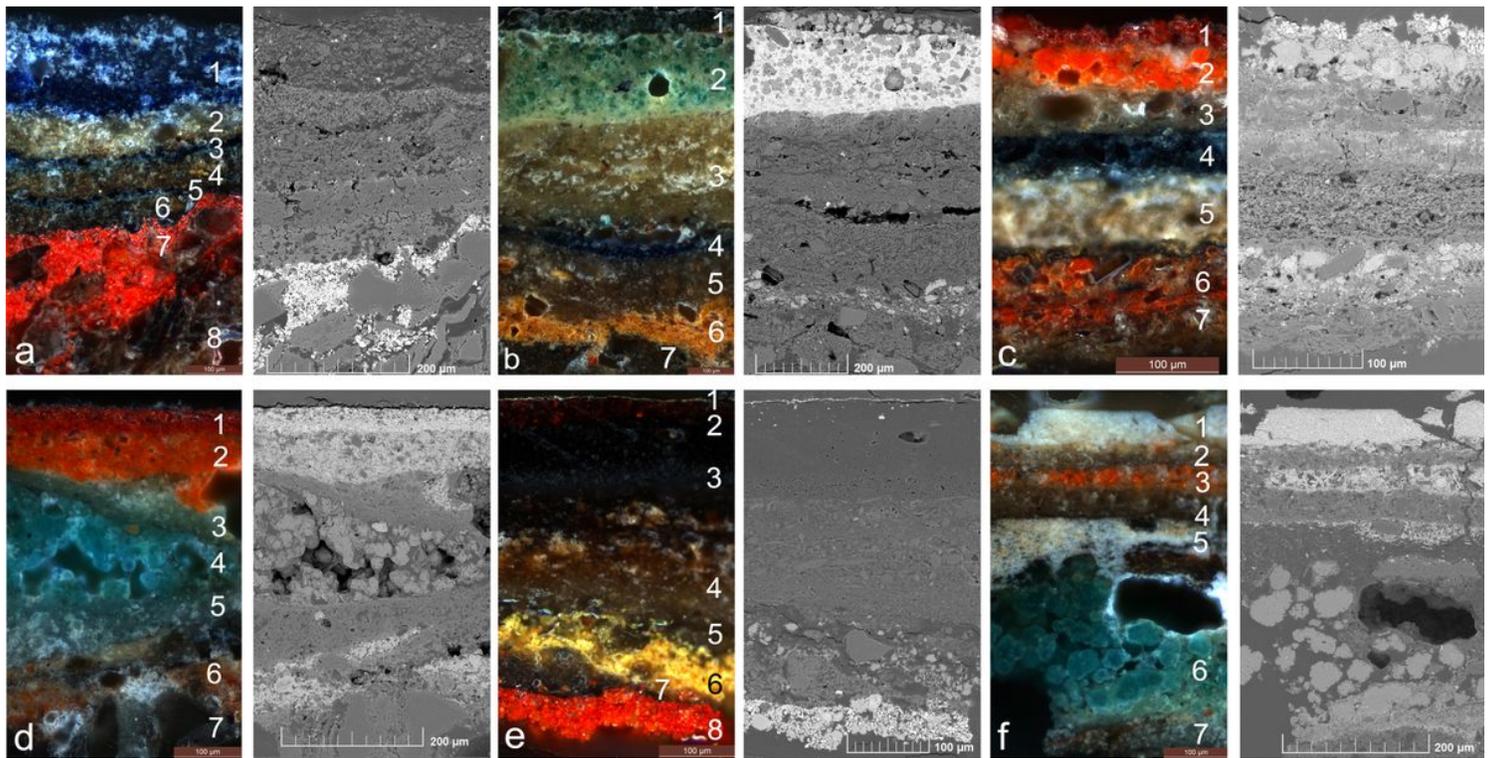


Figure 2

OM and BSE images of cross section samples revealing paint stratigraphy: (a) CS 1, (b) CS 5, (c) CS 10, (d) CS 11, (e) CS 13, (f) CS 16.

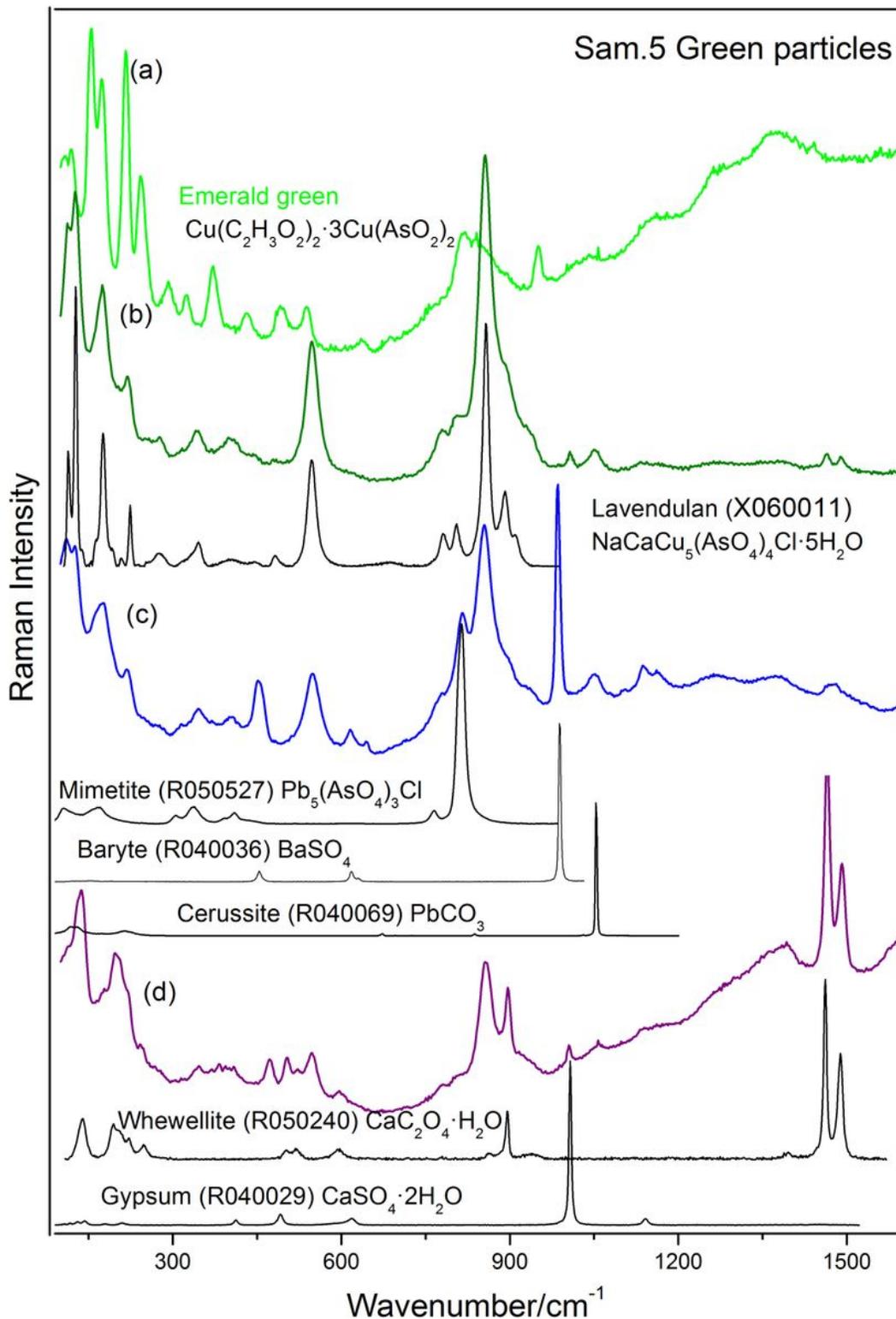


Figure 3

Raman spectrums from green layer (1 and 2 in Fig.2b) of CS 5: (a) ~ (d) show characteristic peaks for emerald green (only in layer 2), lavendulan; mimetite, baryte, cerussite; whewellite and gypsum. Black reference spectrums from RRUFF open database.

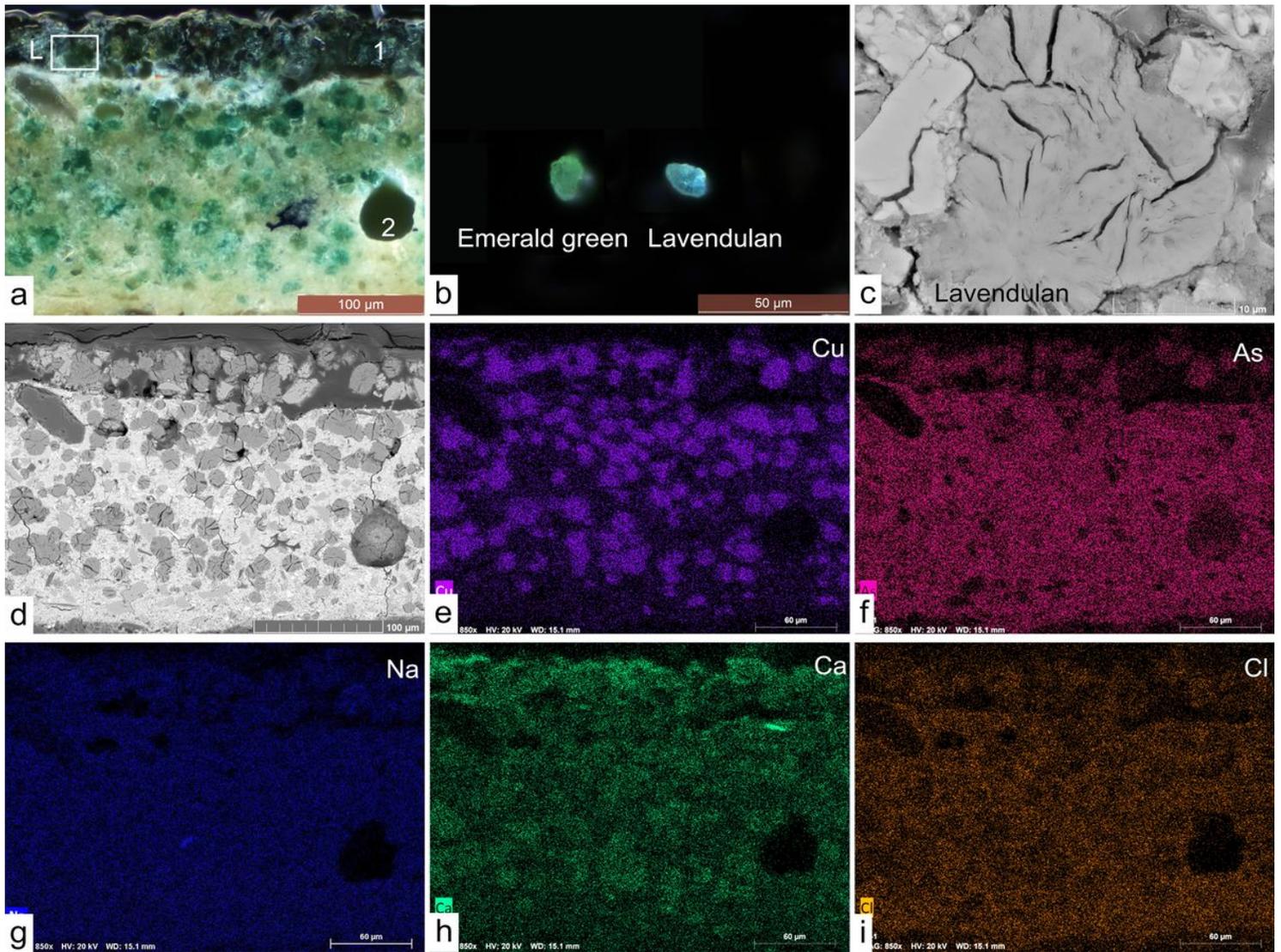


Figure 4

Green layer (1 and 2 in Fig.2b) of CS 5: (a) optical microscopic image of green layer, (b) optical microscopic image of particles show the loss of green coloration of emerald green degraded into lavendulan, (c) SEM-BSE image of lavendulan particles, (d) SEM-BSE image of green layer, and elemental maps of (e) copper, (f) arsenic, (g) sodium, (h) calcium and (i) chlorine show that arsenic migrated out the particle and diffusion within the whole green layers while the occurrence of copper is limited within green particles.

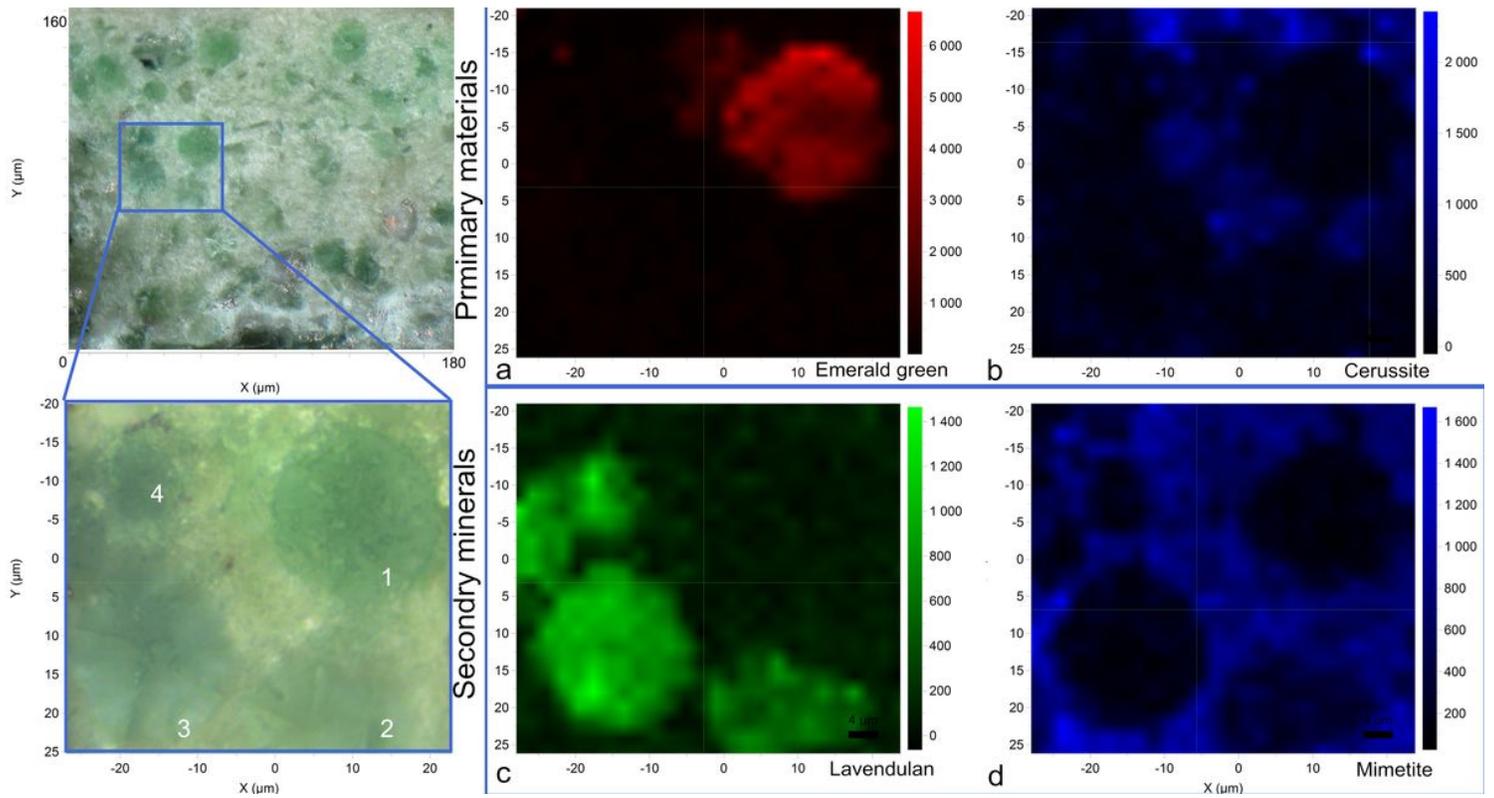


Figure 5

Raman maps of a sub area (see rectangle) of green layer (2 in Fig.2b) of CS 5: (a) Emerald green and (b) Cerussite, assumed to be originally present in green layer; (c) Lavendulan and (d) Mimetite as to secondary minerals, formed in situ.

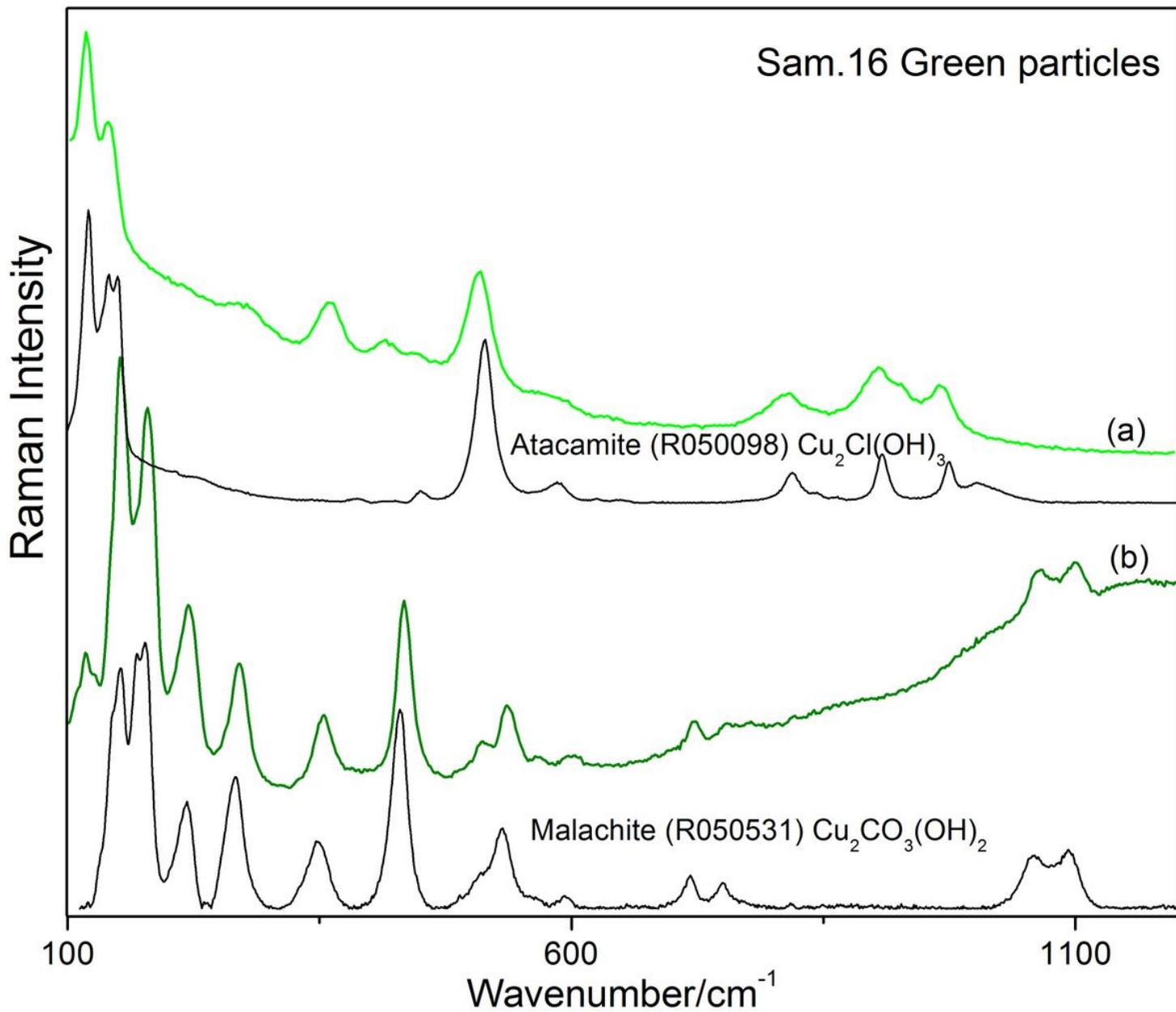


Figure 6

Raman spectrums from green layer (layer 6 in Fig.2f) of CS 16: (a) atacamite and (b) malachite. Black reference spectrums from RRUFF open database.

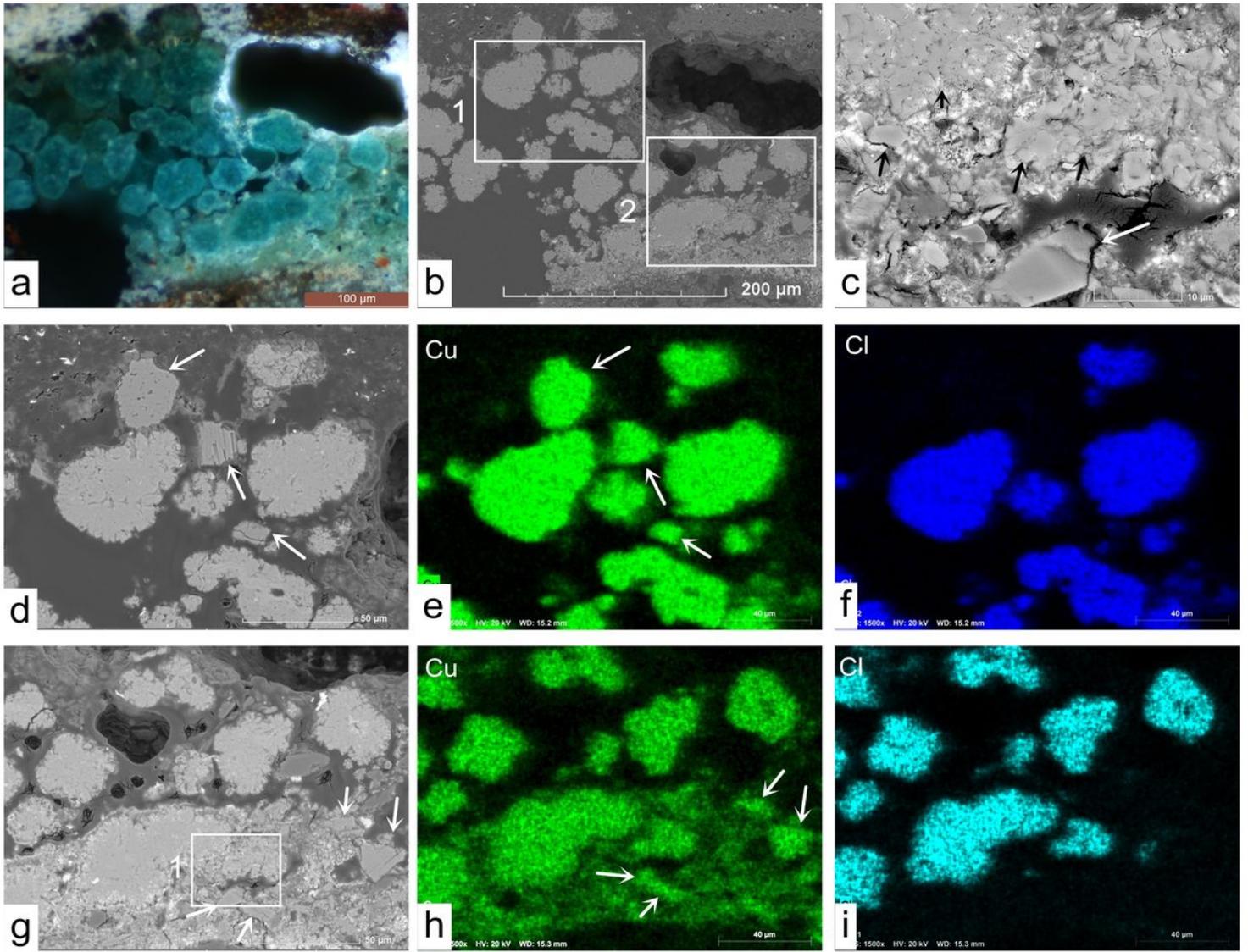


Figure 7

Microscopic images of green layer (layer 6 in Fig.2f) of CS 16: (a) OM, (b) SEM-BSE, (c) BSE image enlarged rectangle