Alteration of azurite into paratacamite at the St. Alessandro Church (Lasnigo, Italy)

Alteração de azurite para paratacamite na Igreja de S. Alessandro (Lasnigo, Itália)

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Abstract

Many case studies report the alteration of the pigment azurite into paratacamite on wall paintings in Europe (for instance in Italy, Portugal, Austria).

The analytical research performed on the 16th century wall paintings in the St. Alessandro church at Lasnigo (North Italy) pointed out an irregular and inhomogeneous alteration of azurite. It is well known that azurite can transform into malachite when the humidity is high and in alkaline conditions and into basic copper chlorides (atacamite, paratacamite, clinoatacamite) when solutions containing chlorine ions are present.

X-ray diffraction allowed to refer the green compounds to paratacamite. The remaining surfaces painted with azurite do not reveal any trace of alteration despite of the presence of chlorine; a few traces of azurite have been found inside the direct incisions of the *Crucifixion* painted scene where the original blue pigment was completely lost.

The microclimatic conditions seem to play an important role in the process in addition to the presence of water and chlorides. The surface where alteration occurs is the only one to be cyclically heated by the solar radiation, causing the transport of the solutions containing chlorides. The relationship between the environment and the chemical processes occurring represents an important issue to be developed.

Keywords

Azurite; Paratacamite; Wall paintings; Lasnigo.

Resumo

São vários os estudos que relatam a alteração do pigmento azurite em paratacamite em pinturas murais na Europa (por exemplo, em Itália, Portugal e Áustria).

O estudo das pinturas murais quinhentistas existentes na Igreja de S. Alessandro, na aldeia de Lasnigo (norte de Itália), permitiu detectar uma transformação irregular e heterogénea da azurite. É do conhecimento geral que este mineral se transforma em malaquite em ambientes com elevados níveis de humidade e em condições alcalinas e se transforma em cloretos básicos de cobre (atacamite, paratacamite, clinoatacamite) na presença de soluções contendo iões cloreto.

Por difracção de raios X foi possível associar os compostos verdes a paratacamite. As restantes superfícies pintadas com azurite não revelaram quaisquer indícios de alteração, apesar da presença de cloretos. Vestígios de azurite foram encontrados dentro das incisões directas na cena da *Crucificação*, onde o pigmento azul original é actualmente inexistente.

As condições microclimáticas parecem ter desempenhado um papel importante no processo, conjuntamente com a água e os cloretos. A superfície onde ocorreu a alteração é a única a ser aquecida ciclicamente pela radiação solar, o que provocou a migração de soluções com cloretos. A relação entre o ambiente e os processos químicos é um importante aspecto que interessa desenvolver.

Palavras-chave

Azurite; Paratacamite; Pintuta mural; Lasnigo.

Introduction

The pigment azurite was used to paint the blue drapes on the 16th century wall paintings (fig. 1) in the St. Alessandro Church at Lasnigo (Como, North Italy).

Fig. 1 St. Alessandro church (Lasnigo, Italy): 16th century wall paintings.

The Crucifixion scene on the east wall of the presbytery painted in 1513 by Andrea De Passeri retains traces of the original pigment. The blue drapes in the Re Magi scene on the north wall of the presbytery painted by Magister Jeronimus in 1547 show the pigment unaltered. The decoration of the chancel arch painted by the latter Master in 1547 revealed an irregular green alteration (fig. 2).

Preliminary non destructive in situ Raman spectroscopy [1, 2] was carried out.

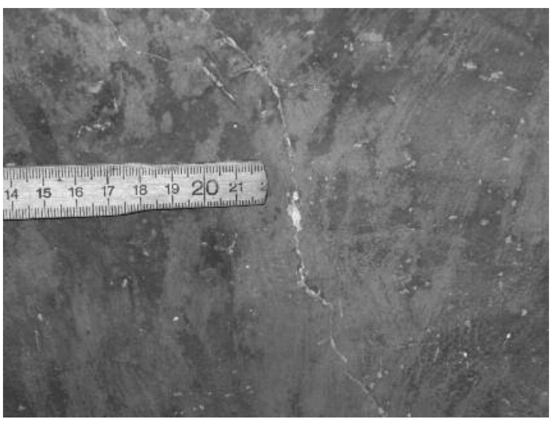

Fig. 2 Irregular and inhomogeneous alteration of azurite into paratacamite.

In this paper, the results obtained using micro destructive analyses (optical and electron microscopy on cross sections, microanalysis and X-ray diffraction) will be presented and discussed.

Materials and methods

Samples of altered and unaltered azurite have been analyzed by means of optical and electron microscopy, microanalysis, X-ray diffraction.

Cross sections have been prepared for stratigraphic observations under microscope in incident light using a Zeiss Axioskop 40.

A VEGA TESCAN electron microscope coupled with an EDS detector was used for the microanalysis of cross sections, operating at the following conditions: 20 kV, vacuum mode HV, WD 9 mm.

X-ray diffraction (XRD) has been employed to identify the mineralogical composition of the green compounds using a diffractometer D8 Bruker; X-ray tube with Cu anti-cathode, Ni filter (Cu $K\alpha$ = 1.5418 Å), generator settings 40kV and 40mA.

Table 1 reports the samples studied. The choice of the samples was made to understand the mineralogical composition of the green compounds (powder of the material was collected from the pictorial surface for XRD) and the differences occurring in terms of chemical composition where the original pigment azurite was altered and unaltered.

Results

Optical microscopy

The cross sections examination under microscope allowed to reconstruct the stratigraphy and the pictorial technique as reported in Table 2. All the studied samples show a typical sequence for the use of azurite on 16th century wall paintings: red ochres with the addition of charcoal black used *a fresco* followed by azurite applied *a secco*.

Table 1 Samples, description and location.

No.	Samples description	Location
1	Virgin Mary's drape close to the alteration of the blue pigment.	South part of the chancel arch, lower part.
2	Virgin Mary's drape (unaltered blue pigment).	South part of the chancel arch, lower part
3	Virgin Mary's drape (unaltered blue pigment)	*Re magi* adoration scene, north wall in the presbytery.
4	Blue pigment	*Crucifixion* scene, east wall in the presbytery.
5	Virgin Mary's drape close to the alteration of the blue pigment.	South part of the chancel arch, upper part.
6	Virgin Mary's drape	South part of the chancel arch, lower part.
7	Virgin Mary's drape, around the head.	South part of the chancel arch, upper part.

Table 2 Stratigraphy under the microscope.

No.	Layers	Optical microscopy (incident light)
1	1	Lime based mortar with the addition of silica-carbonates aggregates, grain size distribution ranging 20-120 μm (*intonachino*).
	2	Red layer obtained using red ochres and charcoal black (*morellone*), thickness ranging 20-50 μm. *Fresco* is the technique used.
	3	Blue layer showing chromatic alterations green in colour, thickness ranging 10-40 μm. The grain size of the pigment is about 5 μm; the maximum grain size is 10 μm and the edges are sharp. The pictorial technique used is *a secco*. Azurite is the pigment used.
2	1	Lime based mortar with the addition of silica-carbonates aggregates, grain size distribution ranging 20-120 μm (*intonachino*).
	2	Red layer obtained using red ochres and charcoal black (*morellone*), thickness ranging 15-20 μm. *Fresco* is the technique used.
	3	Blue layer, thickness ranging 20 -30 μm. The grain size of the pi gment is about 20 μm; the maximum grain size is 50 μm and the edges are sharp. The pictorial technique used is *a secco*. Azurite is the pigment used.
3	1	Lime based mortar with the addition of silica-carbonates aggregates, grain size distribution ranging 50-120 μm (*intonachino*).
	2	Red layer obtained using red ochres and charcoal black (*morellone*), thickness ranging 5-30 μm. *Fresco* is the technique used.
	3	Blue layer, thickness ranging 20 -40 μm. The grain size of the pigment is about 20 μm and the edges are sharp. The pictorial technique used is *a secco*. Azurite is the pigment used.

Table 3 Microanalysis.

No.	Layer	Chemical elemental analysis							
		Fe	Si	S	Ca	Cl	Cu	K	Ba
1	2	+ + +	+	+	+	-	-	-	-
	3	+	+	+	+	+ +	+ + +	-	-
2	3	-	+	+ + +	+ +	+	+	-	+ + +
3	3	+	+	+	+ +	+	+ + +	+	-

Legend: + + + main element; + + subordinate element; + accessory element; - absent or <LOD.

Microanalysis

Table 3 reports the qualitative elemental analysis carried out on the pictorial layers of the samples examined under the optical microscope.

Fe is related with red ochres; Si with the composition of the aggregates; S with sulphates; Ca with the binder (sample 1, layer 2) and with the sulphates (samples 1, 2 and 3, layer 3); Cu and Cl with basic copper chlorides (samples 1, layer 3); Cu with basic copper carbonates and Cl with chlorides (samples 2 and 3, layer 3); Ba was only detected on the third layer of the sample no. 2 and could be related both with Ca (Ba-carbonate) and with S (Ba-sulphate). K was detected as accessory element just on the third layer of the sample no. 3.

X-Ray Diffraction

Table 4 reports the qualitative mineralogical analysis. The presence of quartz is related with silica sands coming from the *intonachino*; calcite with the binder; gypsum as secondary product coming from the dissolution of gypsum-based repair mortars followed by precipitation and re-crystallization; halite has been detected only on the sample no. 7; the basic copper chloride on the altered surface is paratacamite, sometimes associated with unaltered azurite (sample 5); azurite corresponds to the basic copper carbonate (samples 2 and 4); smithsonite was found in the sample no. 5 and hausmannite in the sample 6.

Discussion

The pigment azurite has been used according to the usual practice: a layer of *morellone* (hematite mixed with charcoal black) was applied *a fresco* on the *intonachino* (the final layer of the plaster) as preparation for the blue pigment. Azurite has been applied using the *a secco* (dry) technique mixed with a proteinaceous binder [3]. The grain size of azurite is different; it is similar for samples 2 and 3, ranging from 20 to 40 microns, and quite different for sample 1, where the medium grain size is 5 microns. This difference in the grain size is related to the final tone required where coarsely ground particles produce dark blue and fine ones a lighter tone [4].

Under the microscope, the particles of azurite have the typical broken and fractured appearance [4]; the observations under microscope clearly reveal the different appearance of the azurite being deep blue where unaltered (fig. 3) and showing a green color where altered (fig. 4).

The microanalysis of the third layer, corresponding to the final pigment, shows the presence of chlorine both on the altered and unaltered surfaces. X-ray diffraction on the powder collected from the same layer allowed to detect the presence of paratacamite in the south part of the chancel arch (fig. 5) and of azurite on the north wall of the

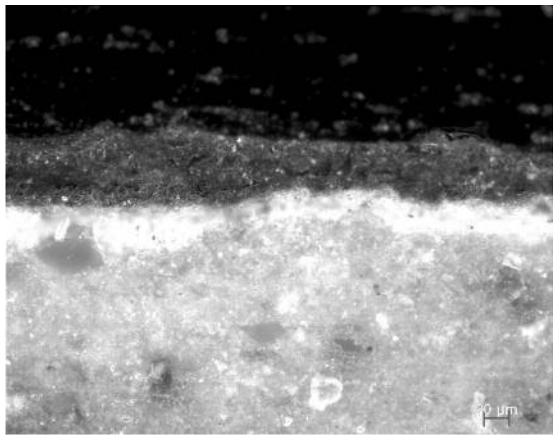

Fig. 3 Cross section of unaltered azurite under incident light (sample no. 3).

Table 4 X-ray diffraction analysis.

No.	Mineralogical phases							
	Qtz	Cal	Gp	Hl	Par	Az	Smit	Haus
2	+	-	+ + +	-	-	+	-	-
4	+	+ + +	+	-	-	+ + +	-	-
5	+	+ +	+ + +	-	+ + +	+	+ +	-
6	+	+	+ +	-	+ + +	+	+	+
7	+ +	-	+ + +	+ +	+ + +	-	-	-

Legend: + + + main mineralogical phase; + + subordinate mineralogical phase; + accessory mineralogical phase; - absent or <LOD
Qtz quartz; **Cal** calcite; **Gp** Gypsum; **Hl** halite; **Par** paratacamite; **Az** azurite; **Smit** smithsonite; **Haus** hausmannite.

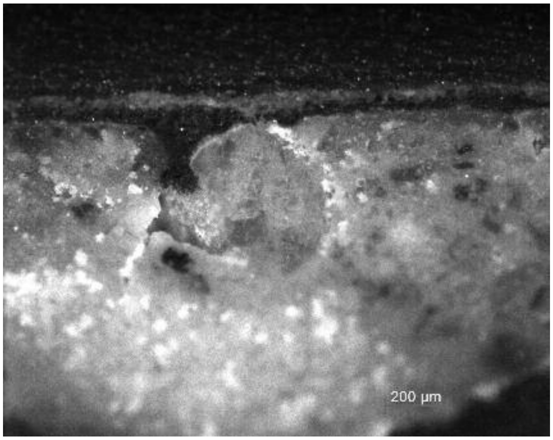

Fig. 4 Cross section of altered azurite under incident light (sample no. 1).

presbytery (fig. 6). Sample 2 shows the presence of barium detected at the surface of the third layer; Ba-compounds in the form of Ba-sulphates and/or Ba-carbonates could be related with restoration treatments [5] and/or be considered as impurity of the copper-based pigment [6].

All the samples show the presence of salts in the form of white veils represented by gypsum $CaSO_4{\cdot}2H_2O$ (all the samples) and halite NaCl (sample 7). Smithsonite $ZnCO_3$ (samples 5 and 6) and hausmannite (sample 6) could be related to impurities of the pigment used [6].

The data agree with the fact that the presence of chloride ions is not sufficient *per se* to determine the alteration of azurite into paratacamite. Other factors such as the presence of water and the possibility of the solution containing chloride ions to migrate from the inside part of the wall up to the surface where the pigment azurite is (evaporation process), should be taken into account for the explanation of the phenomenon [7].

The south part of the chancel arch presents an important structural crack moving from the roof down to the painted surface where the azurite alteration is evident. Archive documentation indicates that, during the 1970s, there was an infiltration of water along this crack. This water caused the passage of the chlorine into the solution. As regards the origin of the chlorine, many causes can be responsible: the addition of chlorides inside original and repair mortars [8], the use of chlorides-bearing products during past restoration works [9], the presence of chlorides as *natural source* inside the wall.

The surface where paratacamite is present is cyclically heated by the direct solar radiation entering the window located on the south wall of the church. This heating could have played an active role in the mechanism governing the nucleation and precipitation of paratacamite during evaporation processes.

Conclusions

The presence of paratacamite on wall paintings as alteration of azurite when solutions containing chlorides ions and under specific microclimatic conditions is not a unique case [10].

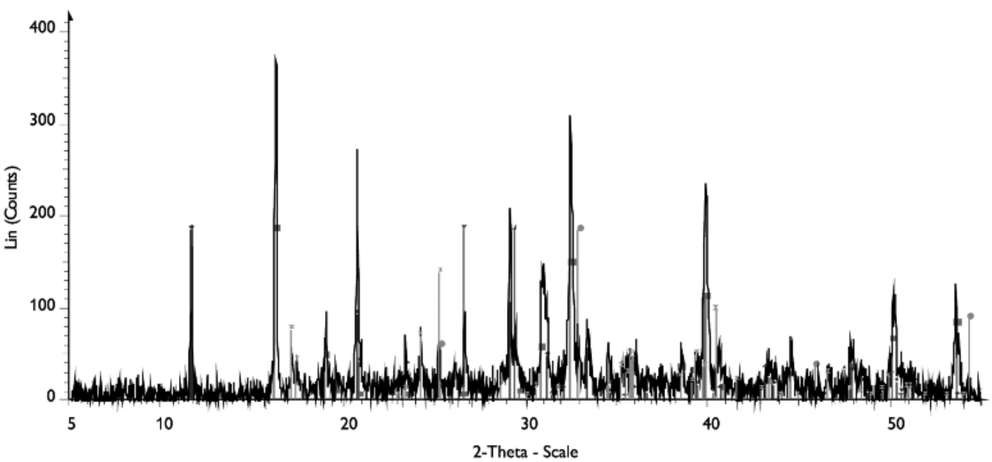

Fig. 5 XRD of the sample no. 5.

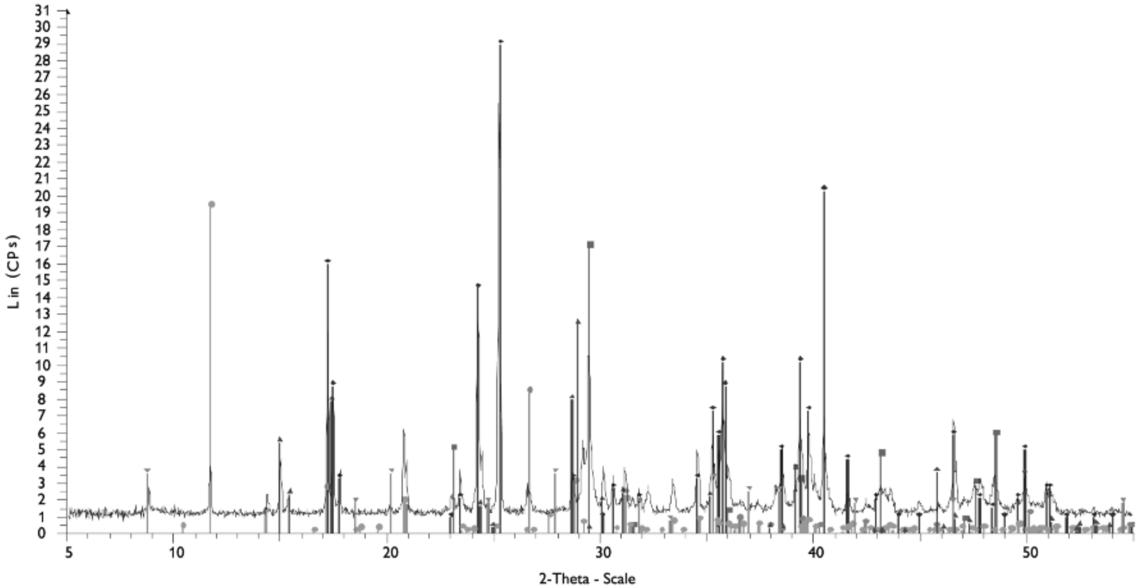

Fig. 6 XRD of the sample no. 4.

All the considered studies agree in considering the alteration is a phenomenon limited to restricted areas, the appearance is inhomogeneous and sometimes paratacamite is associated with malachite.

According to Sharkey and Lewin, the proposed mechanisms for the transformation of azurite can be related to direct precipitation, oxidation product, replacement reaction, indirect precipitation [7].

The case study proposed is very interesting because azurite shows three different states in less than a few linear meters: it is completely lost on the east wall of the presbytery except for a few traces inside the direct incisions; it is well preserved on the north wall of the presbytery; it is altered on the south part of the chancel arch: here the seepage from the roof along the vertical crack, the presence of chlorine and the microclimatic conditions may have a connection in the alteration of azurite. Naturally more experimental works are required to explain how these conditions can determine the observed phenomena.

References

1 Bruni, S.; Guglielmi, V., 'La spettroscopia Raman per lo studio delle opere d'arte', *La chimica e l'industria* **87** (2005) 68-73.

2 Bruni, S.; Guglielmi, V., 'Application of a compact portable Raman Spectrometer for the field analysis of pigments in works of art', in *Lasers in the Conservation of Artworks*, ed. J. Nimmrichter, W. Kautek, M. Schreiner, Springer, Berlin (2007) 407-414.

3 Cavallo, G.; Dal Bianco, E.; Luzzana, G., 'I dipinti murali cinquecenteschi della chiesa di Sant'Alessandro a Lasnigo: nuovi dati sui materiali originali e le tecniche esecutive', in *Colore e Arte: Storia e Tecnologia del Colore nei Secoli*, ed. M. Bacci, Patron Ed., Bologna (2008) 255-264.

4 Gettens, R. J.; Fitzhugh, E., 'Azurite and Blue Verditer' in *Artists' Pigments*, vol. 2, ed. A. Roy, Washington, National Gallery of Art, Washington (1993) 23-35.

5 Dei, L.; Ahle, A.; Baglioni, P.; Dini, D.; Ferroni, E., 'Green degradation products of azurite in wall paintings: identification and conservation treatment', *Studies in Conservation* **43** (1998) 80-88.

6 Seccaroni, C.; Moioli, P., *Fluorescenza X*, Nardini Ed., Firenze (2002) 154-157.

7 Sharkey, J. B.; Lewin, S. Z., 'Conditions governing the formation of atacamite and paratacamite', *The American Mineralogist* **56** (1971) 179-192.

8 Torraca, G., 'Tecnologia delle malte per intonaci e della conservazione degli intonaci antichi', in *Diagnosi e Progetto per la Conservazione dei Materiali dell'Architettura*, Ed. De Luca, Roma (1998) 203-221.

9 Giovannoni, S., Private communication (2007).

10 Bianchetti, P.; Santopadre, P., 'Alterazione dei pigmenti nei dipinti murali: la trasformazione dell'azzurrite in paratacamite', *Bollettino ICR* **8-9** (2004) 76-86.

Received: 14 October 2008
Revised version: 28 April 2009
Accepted: 5 March 2009