Alteration of azurite into paratacamite on wall paintings

O pigmento azurite foi largamente utilizado na pintura europeia durante toda a Idade Média, o Renascimento, e posteriormente. A azurite foi usada para pintar os panos azuis das pinturas murais do século XVI na Igreja de Santo Alexandre em Lasnigo (Como, norte de Itália). A decoração do arco do coro, pintado por mestre Jeronimus em 1547, revelou uma irregular alteração verde. Análises não destrutivas (espectrografia Raman *in situ*) e micro destrutivas (microscópio óptico e de electrões, microanálises e raio-X) foram utilizadas para entender a composição química e mineralógica dos compostos verdes.

INTRODUCTION

The pigment azurite was largely used in European painting during all the Middle Ages, the Renaissance and later [1].
Azurite was used to paint the blue drapes on the 16th century wall paintings in the St. Alessandro Church at Lasnigo (Como, North Italy).
The pigments have been completely lost on the Crucifixion scene on the east wall of the presbytery painted in 1513 by Andrea De Passeri; traces are still present inside the direct incisions. White veils due to sulphates covered the azurite on the *Re Magi* scene on the north wall of the presbytery painted by Magister Jeronimus in 1547; the pigment is unaltered. The decoration of the chancel arch painted by the latter master in 1547 revealed an irregular alteration green in colour (fig. 1).
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.

Fig. 1 - St. Alessandro church in Lasnigo (Como, north Italy), south part of the chancel arch. The blue drapes show an irregular and inhomogeneous alteration of azurite

Non destructive (in situ Raman Spectroscopy) and micro destructive analysis (optical and electron microscopy on cross sections, microanalysis and X-Ray Diffraction) have been carried out for understanding the chemical and mineralogical composition of the green compounds.

ANALYTICAL EVIDENCES

The pigment azurite, mixed with a proteinaceous binder, was applied on a support layer obtained using red earth (hematite) and charcoal black (*morellone*) [2].
Optical microscopy on cross sections shows that the original blue pigment has completely turned into a green one, except for a few grains still blue (fig. 2).
Microanalysis on cross-sections showed the presence of Cl and Cu as main elements: this was clearly related to basic copper chloride minerals, not excluding the presence of malachite and/or other copper green.
In situ Raman spectrometry pointed out the presence of clinoatacamite [3, 4].
The application of X-Ray Diffraction on samples collected from the chancel arch in St. Alessandro church (Lasnigo) showed the presence of paratacamite (fig. 3). Paratacamite is also reported in experimental works carried out on other Italian wall paintings (Scrovegni Chapel, Padua; the St Magno Cave in the Cathedral of Anagni; the New Chapel of St. Brizio Chapel at Orvieto's Dome; Cimabue wall paintings at Assisi). In all this cases paratacamite is the main phase detected, sometimes associated with malachite, always in traces [5]. The transformation of azurite into paratacamite has been also referred in Austrian churches.

DISCUSSION AND CONCLUSIONS

All the case studies reported confirm that the alteration of azurite into paratacamite is located on limited and inhomogeneous areas and is due to solutions containing chlorides. The origin of chlorides may be related to different causes such as the addition of $CaCl_2$ into the origi-

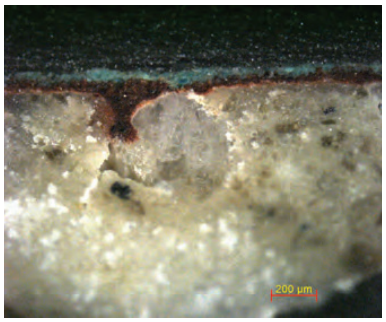

Fig. 2 - Cross section under optical microscope showing the complete transformation of azurite into paratacamite except for a few grains

Fig. 4 - St. Alessandro church in Lasnigo (Como, north Italy), south part of the chancel arch stricken by the solar radiation from the window

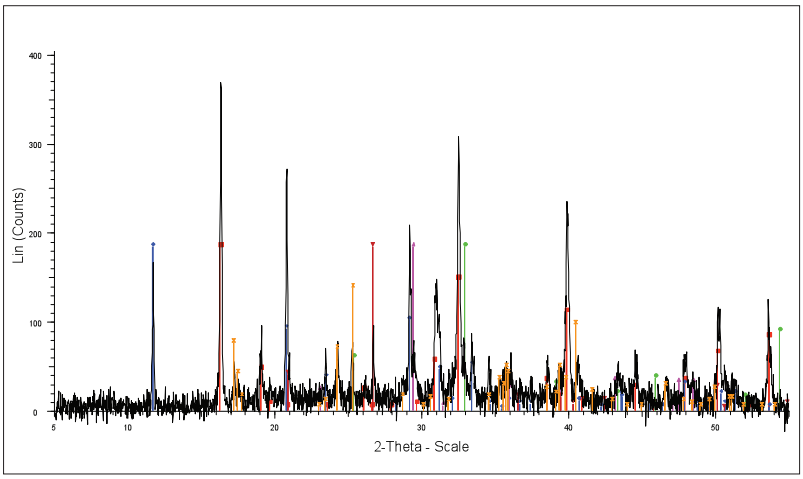

Fig. 3 - XRD of the green alteration product; paratacamite is the main mineralogical phase (red line) followed by gypsum (blue), smithsonite (green), calcite (pink), quartz (brown), azurite (orange)

nal and/or repair mortars to speed up the hardening process [6]; as well as the addition of alkaline products into cementitious repair mortars [7] and like products used in the past restoration works for cleaning the surfaces (diluite HCl or strongly chlorinated water) [8].

A few cases refer the presence of malachite; this could suggest that malachite is an intermediate product accompanying the final transformation into paratacamite following the replacement reaction proposed by Sharkey J.B. and Lewin S.Z. [9]:

$$Cu_2(OH)_2CO_3 \text{ (malachite)} + Cl^- + H_2O = Cu_2(OH)_3Cl \text{ (paratacamite)} + HCO_3^-$$

The nucleation and growth of paratacamite occurs under conditions of low $CuCl_2$ concentration and it deposits slowly; the replacement of CO_3^{2-} in malachite by Cl^- and the indirect precipitation by or on calcite in chloride solution, all result in the production of pure paratacamite when the $CuCl_2$ concentration is sufficiently small [9].

The microclimatic conditions seem to play an important role; considering the surfaces where azurite is still present at the St. Alessandro church in Lasnigo, chlorine has been detected both on the north wall of the presbytery (unaltered azurite) and on the south part of the chancel arch (altered azurite).

Paratacamite formed where water was available - during the Seventy years of the last century there was a seepage from the roof along an important crack - and evaporation processes active probably influenced by the cyclic solar radiation entering the church from the window of the south wall (fig. 4).

The alteration of azurite into paratacamite on wall paintings may be considered not an isolated case, probably due to an insufficient analytical investigation.

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NOTA

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