Study of damage induced by ion beam in white pigments

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Abstract. Pigments and paint layers are known to be sensitive to particle irradiation. Occasionally, the analysis of paintings by PIXE can induce a slight or dark stain depending on the irradiation conditions. In order to understand the damage formation, we have irradiated white pigments (lead white, basic lead sulphate, calcium sulphate, gypsum, calcite, zinc oxide, titanium oxide and lithopone) with the external 3 MeV proton micro-beam used for PIXE experiments. We have observed various sensitivities according to the pigment; for the majority of the studied compounds, the damage is proportional to the beam current and the charge, but for other compounds the behavior is different. For example, no visible change occurs for calcite but, on the other hand, lead white pigments seem to be very sensitive. Damages induced by the proton beam were studied by micro-Raman spectrometry. Structure modifications, such as dehydration, were detected, specially for lead compounds. The damage recovery was investigated by heating and UV-light irradiation. Damage disappeared after one week of illumination UV, showing that PIXE experiments can be safely undertaken for pigments.

Keywords: White pigments, damage, beam irradiation, Raman spectroscopy, annealing, UV treatments.

INTRODUCTION

The particle induced X-ray emission (PIXE) analytical technique is very widely used for the study of art works and archaeological items[1,2,3]. Occasionally, the beam irradiation generates a "dark spot" on some sensitive materials and in particular in some kind of pigments, limiting its application for fragile works such as painted works.

There are few studies on the formation of dark spot published in the literature. In the first work Absil *et al.*[4] applied a proton beam with an intensity lower than 1 nA to carbonate pigments (lead white and calcium carbonate) and they assigned the production of the stain to the formation of colour centres. They also concluded that the dark spot was a totally reversible phenomenon and that no molecular changes were induced by the irradiation.

Enguita *et al.*[5] used ionoluminiscence combined with PIXE during the irradiation to study the production of damage in carbonate minerals (calcite, dolomite, cerusite, malachite and azurite) by proton irradiation using a beam current of 130 pA. After

irradiation, they employed thermoluminescence and optical absorption techniques to study the possible formation of colour centres. They observed the formation of characteristic electron traps during the irradiation and that the impurities act as recombination centres.

The present work has been concentrated in the understanding of the damage process induced on white pigments, with emphasis on lead white, historically the most important of all white pigments[6]. In order to estimate the risk of damage, we have performed a study of the influence of the charge and of the beam current. Furthermore, two methods for damage recovery, namely annealing and UV illumination, were applied to the lead white pigment which was found to be the most prone to formation of the dark spot.

EXPERIMENTAL SET UP

Sample Description and Irradiation

The materials selected for this work include white pigments used commonly in paintings[7]: zinc oxide (ZnO), titanium oxide (TiO_2), lithopone (mixture of barium sulphate ($BaSO_4$) and zinc sulfide (ZnS)), calcium carbonate ($CaCO_3$) and different lead white compounds ($PbSO_4.3PbO.H_2O$, $2PbCO_3.Pb(OH)_2$, $PbSO_4$, and $PbCO_3$). In order to compare the anion influence in the damage we also irradiated calcium sulphate ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$). All materials used in the present work were previously characterized by X-ray diffraction (XRD).

The pigment samples have been irradiated with the external micro-beam of the AGLAE facility of the C2RMF[8,9] using a 3 MeV proton beam of 30 μm diameter. Targets were positioned at 3 mm from the exit window and scanned with a motorized sample holder. Beam currents ranging from 0.2 to 4.5 nA and charges between 0.1 and 1.5 μC were applied.

In order to perform the study of the damage recovery, $PbSO_4.3PbO.H_2O$, $2PbCO_3.Pb(OH)_2$ and $PbCO_3$ pigments were selected and irradiated over an area of 500 x 500 μm^2 by scanning the sample with beam current of about 1.6 nA and total charge of 0.6 μC.

Experimental techniques

After proton irradiation, the samples were examined by optical microscopy and those ones with a visible dark spot were selected. The pigments chosen for the second phase of the study were: $PbSO_4$, $PbSO_4.3PbO.H_2O$, $2PbCO_3.Pb(OH)_2$, and $PbCO_3$.

Raman spectra were obtained with a Jobin Yvon HORIBA[10] micro-spectrometer to determine the possible changes at the molecular level. Laser wavelengths of 531.95 or 635 nm were used with the purpose of selecting the better spectrum. A line-scan was performed to measure a series of 12 spots every 9 μm on the samples, from the no-irradiated area to the

dark mark.

Methods for the damage recovery

After proton irradiation, two different treatments were applied to study the potential damage recovery: (i) the samples were annealed in air at 70 ºC for 60 hours and (ii) UV illuminated for 130 hours with an OSRAM L36W/73 lamp, the sample placed 10 cm from the lamp were irradiated by UVA radiation (350–400 nm) with a power density of 10 mW/cm^2. These are the only two methods that have been used in pigments for the study of damage recovery in previous works[4].

RESULTS AND DISCUSSION

Micro-Raman spectroscopy

The Raman spectra recorded on the sample $PbSO_4.3PbO.H_2O$ are shown in Fig 1. Spots 1 to 12 in the photograph correspond to the different Raman spectra acquired from the no-irradiated area to the centre of the mark.

The characteristic band of the $PbSO_4.3PbO.H_2O$ compound at 963 cm^{-1} was identified. In the spectra it can be clearly seen a decrease of this peak, whereas the band at 978 cm^{-1} assigned to $PbSO_4.PbO$, $PbSO_4$ and the peak at 541 cm^{-1} attributed to $2PbO.PbO_2$ increased when going towards the centre of the mark (spot 12). This could be interpreted as a molecular change from Pb^{+4} ($PbSO_4$) to Pb^{+2} (PbO_2) in the irradiated zone.

The typical OH band at 3580 cm^{-1} reveals the presence of H_2O. Its drop in intensity would indicate a dehydration process.

In general for the lead white a decrease of the $PbSO_4$ or $PbCO_3$ peak is found to occur with a simultaneous increase of the lead oxide (PbO_2) peak, possibly revealing a molecular change for the oxidation of the samples. In addition, in all irradiated samples a dehydration process is evidenced.
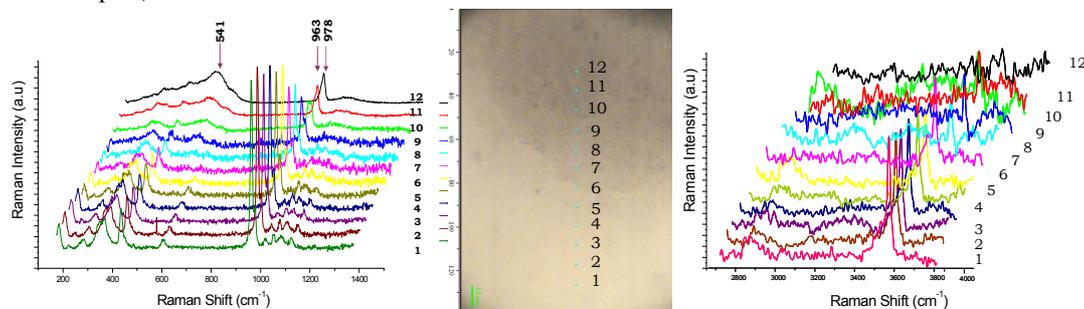

FIGURE 1. Raman spectra of $PbSO_4.3PbO.H_2O$. In the left side, the interval from 200 to 1400 cm^{-1} and in the right side from 2000 to 4000 cm^{-1} is shown. A photograph of the pigment sample with the measured points is shown.

Cooper *et al.*[11] reported the presence of similar marks using laser irradiation instead of proton irradiation of lead white ($2PbCO_3.Pb(OH)_2$), and they attributed its formation to the conversion of basic lead carbonate to elemental lead and lead (II) oxide.

In addition, a strong fluorescence was observed in all Raman spectra with a higher intensity towards the centre of the stain. Absil *et al.*[4] attributed this fluorescence to the de-excitation of colour centres since they absorb visible light and emit in the near infrared spectrum.

Charge and mark relationship

In order to minimise the dark spot generation the qualitative relationship between deposited charge and mark intensity was observed.

The sensitivity of pigment to irradiation is shown in table 1. Different behaviors were found. Lead whites were clearly the most influenced by the beam irradiation, producing easily the darkening spot phenomenon.

TABLE 1. Sensitivity of pigments to irradiation.

No Mark	Light Mark	Strong Mark
$CaCO_3$	$CaSO_4$	Lead white
Lithopone	ZnO	
TiO_2		

A rough proportional relationship between the deposited charge and the mark intensity was estimated by visual observation.

The mark production is also affected by the beam current, being more intense for higher currents. This could be attributed to the increase of the local temperature during the irradiation process.

Damage recovery

TABLE 2. Photograph of the lead white pigments after irradiation and after annealing process.

Pigments	After irradiation	After annealing
$PbSO_4.3PbO.H_2O$		
$PbCO_3$		
$2PbCO_3.Pb(OH)_2$		
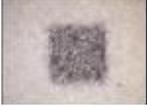
Table 2 shows the photograph of three pigments subjected to annealing treatment (70 ºC for 60 hours). It can be seen a clear partial vanishing of the mark, despite of the moderate temperature. It is expected that a higher temperature would enhance the efficiency of the annealing process since the activation energy will be exceeded by a significant amount. Nevertheless, normally this procedure cannot be carried out on real paintings, given the risk of damage by heat of these fragile and precious works.

Table 3 shows the photograph of the three pigments subjected to the UV treatment (130 hours in a dark purple tube). The results of this process were successful, since the mark disappeared completely from one of the pigments ($PbCO_3$) and almost completely vanished from the other two pigments ($PbSO_4.3PbO.H_2O$ and $2PbCO_3.Pb(OH)_2$). An advantage of the UV illumination is the possibility to apply it to paintings, because art historians already use routinely this kind of light for examination.

TABLE 3. Photograph of the lead white pigments after irradiation and after UV treatments.

Pigments	After irradiation	After UV light treatment
$PbSO_4.3PbO.H_2O$		
$PbCO_3$		
$2PbCO_3.Pb(OH)_2$		

CONCLUSION

The irradiation by protons produces in some white pigments the namely dark spot (specially in lead white pigments). Raman measurements on lead white pigments have shown a possible molecular change and a dehydration process. On the other hand, the fluorescence behavior observed in the Raman spectra can be attributed to the formation of colour centres.

A qualitative proportional relationship between the deposited charge and beam current with the intensity of the mark was observed.

A partial recovery of the damage has been obtained by annealing process and the almost complete vanishing of the mark was observed after UV illumination. This last treatment paves the way to the application of PIXE to the analysis of paint works.

ACKNOWLEDGMENTS

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