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## Modelling and IR thermal monitoring of the laser reconversion of blackened pigments

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### ABSTRACT

Some mural painting pigments tend to blacken with time due to their conversion to dark degradation products. An interesting approach of restauration involving continuous wave Nd:YAG lasers was suggested more than ten years ago, focusing on the reconversion of black plattnerite ( $\beta\text{-PbO}_2$ ) to red minium ( $\text{Pb}_3\text{O}_4$ ). In the context of extending this approach to other pigments concerned by blackening (lead white and cinnabar), the laser heating of plattnerite was monitored by IR camera and modelled. An irradiance threshold (around  $80 \text{ kW m}^{-2}$ ) corresponding to the considered reaction temperature has been measured. A spectrophotometric study was conducted, which unravelled the reflectance changes occurring during the reconversion. Optical and thermal parameters of the plattnerite were measured or extrapolated to run the model. The latter was successful in reproducing the surface temperature evolution only in the first moments of the irradiation.

### KEYWORDS

plattnerite | Nd:YAG | laser heating | mural paintings | restauration

### INTRODUCTION

During the last few decades, Nd:YAG lasers have been increasingly used in the field of cultural heritage restauration due to their costs, portability and ease of use with an optical fibre. Q-switched lasers are mainly used for cleaning by ablation of artefacts (Siano *et al.*, 2012) but continuous wave (CW) lasers have recently drawn attention for their ability to perform reconversion of blackened minium (Aze *et al.* 2007). If the same technique could be used for the reconversion of other degraded pigments used in mural paintings, such as lead white or red cinnabar, it could lead to the development of a new restauration tool, with the same advantages as Q-switched laser that are currently used for cleaning buildings. In that respect, the ability to monitor and model the laser heating of blackened pigments is a first step to evaluate the use of CW laser to other thermally-induced reconversion reactions.

Plattnerite ( $\beta\text{-PbO}_2$ ) is the black degradation product of red lead, or minium ( $\text{Pb}_3\text{O}_4$ ) and of lead white (a mixture of hydrocerussite ( $2\text{PbCO}_3\cdot\text{Pb(OH)}_2$ ) and cerussite ( $\text{PbCO}_3$ )). These pigments were vastly used in mural paintings and yet blackening occurrences are numerous (Aze *et al.*, 2008; Lussier and Smith, 2007). In air, plattnerite is reduced to minium above  $375 \text{ }^\circ\text{C}$  (Clark *et al.*, 1937) and minium is itself reduced to massicot ( $\beta\text{-PbO}$ ) above  $552 \text{ }^\circ\text{C}$  (Ciomartan *et al.*, 1996). Aze *et al.* (2007) have shown that CW Nd:YAG or Ar+ laser heating of plattnerite induces the reconversion reaction to minium and even to massicot if the laser power is high enough. This phenomenon is also observed during Raman analysis of plattnerite samples (Burgio *et al.*, 2001; Costantini *et al.*, 2020).

Here, we demonstrate the importance of monitoring the temperature rise induced by the laser during reconversion experiment. The latter have been reproduced and the samples measured by spectroradiometry. The laser-induced heating was monitored by an IR camera. An attempt at modelling it to gain information inaccessible by standard measurements, for example in-depth or radial temperature profiles, is also described here.

### EXPERIMENTS

Aze *et al.* (2007) experiments have been reproduced: a fibered Manlight ML50 CWR-TKS Nd:YAG laser, with a Gaussian-shaped beam of 1740  $\mu\text{m}$  radius ( $1/e$  value), was directed onto plattnerite pellets. The latter have been obtained by pressing 97 % pure commercially available plattnerite at 100 kN for 10 min, resulting in ca. 400  $\mu\text{m}$  thick pellets. The power of the laser (controlled with a Fieldmate laser power meter and a Coherent powermax PM30) was increased until changes of colours corresponding to the reconversion reactions yielding minium then massicot were observed. The mean laser irradiance was calculated on the  $1/e$  beam surface. We monitored the surface temperature of the samples during laser irradiation with a FLIR SC640 IR camera equipped with a T197089 ( $f = 38$  mm) objective, operated by the ThermaCam software and located 50 cm away from the sample. Its spectral measurement range is [7.5; 13]  $\mu\text{m}$ .

An Olympus SZX7 stereo microscope equipped with a UC30 camera run by the Stream Basic software was used to take pictures of the samples. A RUBY spectroradiometer was then used to acquire the specular reflectance spectra in the [400; 800] nm of the samples and to calculate their colorimetric coordinates in the CIE 1964 space with a D65 illuminant. A Labsphere certified white reflectance standard was used as the white reference and a black cardboard was used as the black reference. For each measurement, 100 spectra were acquired at an 840 Hz rate and averaged. Lastly, Internationale Beleuchtungskommission (2004) formula were used to calculate the RGB values of samples from the  $L^*a^*b^*$  coordinates.

In order to model the laser heating, some thermal and optical properties of plattnerite must be known. Its thermal diffusivity was approximated from surface temperature falls measurements. Its specific heat capacity was measured by differential scanning calorimetry (DSC) with a Netzsch ST409PC device operating at  $2^\circ\text{C min}^{-1}$  and temperature- and sensitivity-calibrated with the following standard elements: In, Sn, Bi, Pb, Zn. Measurements were made on an empty crucible to establish a baseline, then on Al and  $\text{PbO}_2$ . The specific heat capacity of  $\text{PbO}_2$  was then calculated according using the  $C_p$  value of Al at  $300^\circ\text{C}$  given by Netzsch (ref. "TPRL books"). The reflectance of plattnerite at 1064 nm was determined with an integrating sphere (Labsphere), a low power Nd:YAG laser yielding a 12 mW beam and a photodiode connected to a Setaram 5702 oscilloscope. Lastly, these parameters were used to run a 3D analytical model of the heating of materials absorbing energy from an incident laser beam that was previously developed at the CEA Saclay (Semerok *et al.*, 2007).

### RESULTS AND DISCUSSION

We first determined the irradiance threshold at which the plattnerite-to-minium reconversion happens. A plattnerite pellet was irradiated in the [16; 106]  $\text{kW m}^{-2}$  range with 10 to 20  $\text{kW m}^{-2}$  steps for around one minute for each step and cooled down until ambient temperature between two steps. Reconversion to minium was witnessed by observing the sample with the naked eye and noticing a colour change from black to red. It happened between 68 and 86  $\text{kW m}^{-2}$ , which is in the same order of magnitude than what was found by Aze *et al.* (2007): a threshold slightly above 87  $\text{kW m}^{-2}$ .

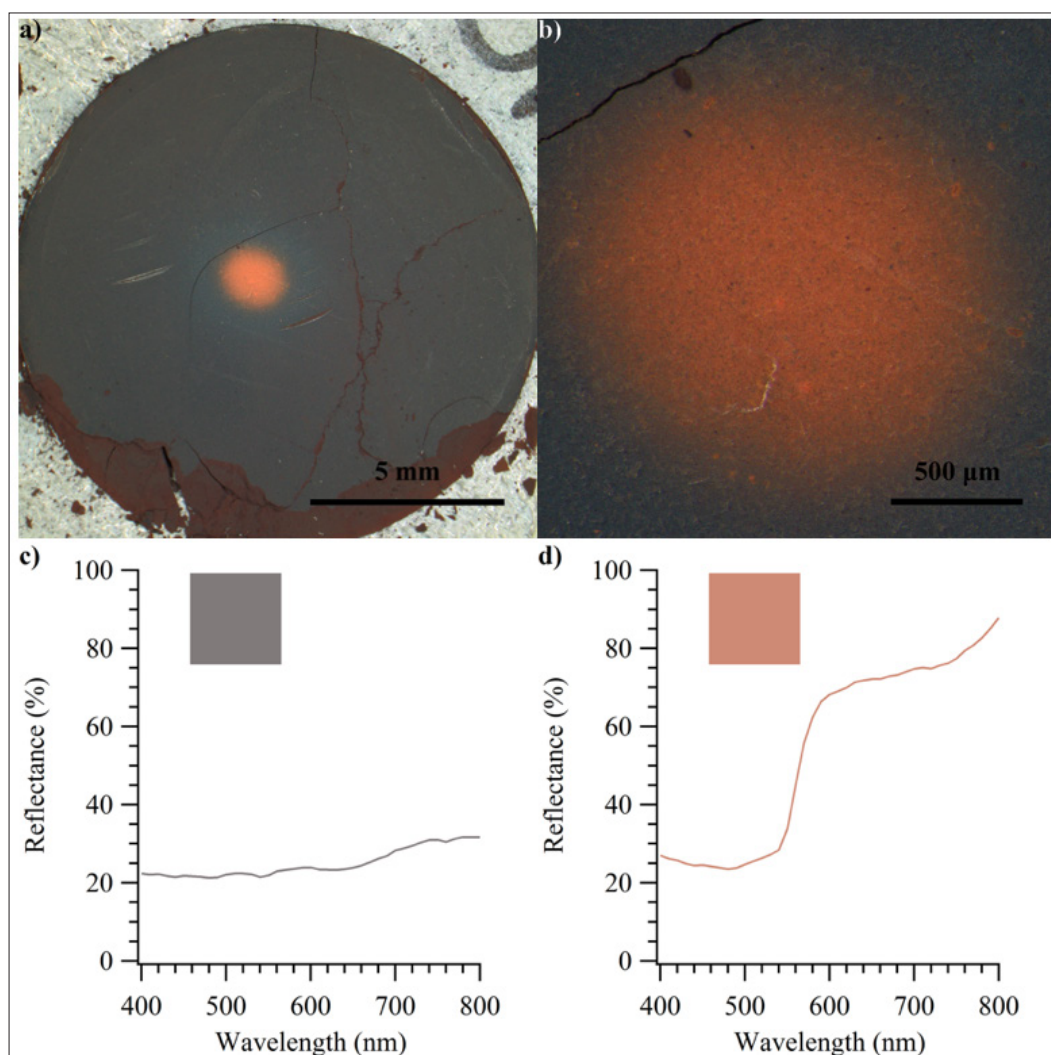


Figure 1: pictures of an irradiated polished plattnerite pellet (a and b, white balance has been performed with the Labsphere white standard) and specular reflectance spectra (c and d) of pristine (c) and irradiated (d) areas after laser irradiation at  $103 \text{ kW m}^{-2}$  for a few minutes. Insets in figures 1c and d display the RGB colours calculated according to the  $L^*a^*b^*$  values.

Figure 1a and b show pictures taken with the stereo microscope of an irradiated plattnerite sample. The reconverted area is clearly visible on figure 1b, appearing as a  $830 \mu\text{m}$  radius quasi-circular homogeneous red/orange spot. The colour change can be appreciated by looking at the reflectance spectra and the colorimetric coordinates displayed on figure 1c and d. There is a clear reflectance increase above  $570 \text{ nm}$  for the reconverted sample (figure 1d), which is consistent with the spectrum of pure minium published by Aceto *et al.* (2014). On the other hand, the pristine sample's spectrum is almost flat in the visible range (figure 1c). The spectrum's flatness explains the very low chroma ( $C^*$ , the coordinate in the equivalent cylindrical system  $L^*C^*h^\circ$ , representing the relative saturation) of the black sample. Conversely the  $a^*$  value has increased for the reconverted sample which reflects its redishing. However, the  $b^*$  has also increased, reflecting a yellowing of the sample. Overall, these changes are well perceptible when looking at the insets of figures 1c and d showing the samples colours calculated from the spectrum.

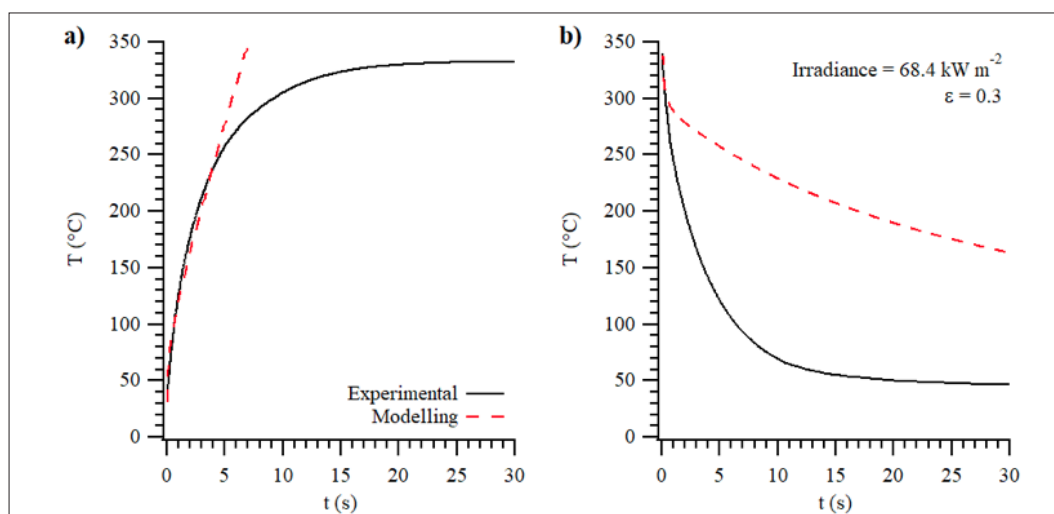


Figure 2: Measured (black full lines) and modelled (red dashed lines) surface temperature rises during laser irradiation at a  $68.4 \text{ kW m}^{-2}$  irradiance (2a) and falls from maximum temperature reached during irradiation (2b) of a  $317 \mu\text{m}$  thick plattnerite pellet.

We then monitored the temperature rises and falls during laser irradiation with the IR camera, with the emissivity set to 0.3, according to the value reported by Schmidt (1979). Black full lines in figure 2 show the evolution of the maximum temperature in the irradiated area during irradiation at a  $68 \text{ kW m}^{-2}$  irradiance, which is just below the reconversion threshold. The time origins of the rise (figure 2a) and of the fall (figure 2b) were taken respectively at laser's on and off switching. On figure 2 we can see that the temperature rises to a max temperature of  $342.8 \text{ }^\circ\text{C}$ , which is a few tenth of degrees below the  $\text{PbO}_2 \rightarrow \text{Pb}_3\text{O}_4$  reaction temperature determined by Ciomartan *et al.* (1996). This result thus confirms that the reconversion takes place above a certain irradiance threshold associated to the reaction temperature, around  $80 \text{ kW m}^{-2}$ . The characteristic time of the temperature rise is 6.6 s and that of the temperature fall is 3.6 s. These are coherent with the observation made by Aze *et al.* (2007) that at  $87 \text{ kW m}^{-2}$ , the reconversion begins after 5 seconds of laser irradiation.

Plattnerite's thermal diffusivity was roughly estimated from the pellet's thickness ( $317 \mu\text{m}$ ) and the temperature fall's characteristic time and a value of  $2.79 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$  was found. This is a coherent first approximation, although a bit low, that will later be validated by the novel photothermal radiometry technique described by Pham Tu Quoc *et al.* (2014). In order to model the laser heating using the code previously developed at CEA Saclay and described elsewhere (Semerok *et al.*, 2007), the following data were also needed. DSC measurements on  $\text{PbO}_2$  gave a result of  $0.490 \text{ J g}^{-1} \text{ K}^{-1}$  for the specific heat capacity.  $\text{PbO}_2$  density is 9.56 according to White (1933) and thus its thermal conductivity is  $0.131 \text{ W m}^{-1} \text{ K}^{-1}$ . Its absorption coefficient at 1064 nm was approximated from Zeyada and Makhlouf (2016) measurements on  $\alpha\text{-PbO}_2$  and a value of  $4.37 \cdot 10^6 \text{ m}^{-1}$  was taken. We measured a reflectance value at 1064 nm of 0.08 using the integrating sphere on a pure and polished  $\text{PbO}_2$  pellet.

The code was then used to model a 30 s irradiation, resulting in the temperature rise displayed in dashed red on figure 2a. During the first 5 s, the model describes accurately the evolution of surface temperature. However, the temperature stabilization that was measured experimentally is not reproduced by the theoretical modelling. This is likely due to the fact that this model does not take the conduction, convection and radiation phenomena into account and most likely the two formers, based on estimations of their relative contribution. These can be of great importance in the long timescale and large irradiated area considered here, as pointed out by Ready (1971). These are probably responsible for the temperature stabilization that is experimentally observed during temperature rise. The modelled temperature fall displayed on figure 2b in red dashed line was shifted so that both experimental and modelled origin temperature are the same. We observe that the modelled surface temperature is higher than the measured temperature. The same explanation can be applied, as conduction, convection and radiation would lower the temperature if they were taken into account.

## CONCLUSION

We successfully reproduced Aze *et al.* (2007) experiment and results, and determined more accurately the laser irradiance threshold (around  $80 \text{ kW m}^{-2}$ ) at which the black plattnerite to red minium reaction takes place. We also characterized scrupulously the reflectance changes occurring during the reconversion. Knowledge on the irradiance dependence of the surface temperature is critical for our forthcoming experiments on the reconversion of plattnerite to lead white. Here we demonstrated the possibility of using an IR camera for such a determination. Then we measured or extrapolated some optical and thermal properties of plattnerite: its specific heat capacity and thermal conductivity, its reflectivity and absorption coefficient at 1064 nm. These were used to model the surface temperature rise and fall of a plattnerite pellet during irradiation. The model that we used reproduced successfully the temperature rise in the first 5 s of the laser irradiation. However, lacking taking into account conduction, convection and radiation phenomena, it does not reflect the temperature evolution after that. This points out the necessity of taking these terms into account for a proper modelling, which can be of great interest. As an example, calculating radial and in-depth temperature profile can explain some aspects of the reconversion experiments at positions that cannot be reached by IR camera monitoring.

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