Continuous wave laser thermal restoration of oxidized lead-based pigments in mural paintings

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Abstract

Red lead and lead white are some of the most ancient and common pigments in mural paintings. However, they tend to blacken with time due to their oxidation to plattnerite (β-PbO2). The possibility to induce the reconversion reactions by CW laser heating is hereby discussed. A thermodynamic study by TGA showed that direct cerussite or hydrocerussite formation from plattnerite are not suitable reconversion routes, which was confirmed by laser irradiation trials under CO2 and CO2/H2O fluxes. Minium (Pb₃O₄) and subsequent massicot (β-PbO) formation from plattnerite were achieved (confirmed by SEM–EDS, XRD and micro-Raman) under Ar+, 810 nm diode and Nd:YAG lasers. The latter appears to be the most suited for restauration purposes, given the broad minium reconversion irradiance range. This is confirmed by successful trials on macroscopic areas of naturally darkened red lead containing samples.

1 Introduction

Of the many pigments that were used in easel as well as in mural paintings, lead-based pigments, particularly red lead and lead white, are definitely the earliest and most widespread [1, 2]. However, when used in mural paintings, they tend to blacken with time, which has been known for a long time [2–4], causing a visual imbalance that can ruin the aesthetic of the artworks [5, 6]. Oxidation to plattnerite seems to be in cause [6–17] in numerous murals [17–29]. Experimental lead white restoration treatments involving chemical reagents to achieve the reconversion have been used [30, 31], but they put the pictorial layers supports at risks as recent research shows [15–18]. Besides, continuous wave Nd:YAG and 810 nm diode lasers were proven to be suitable tools for the thermal reconversion of blackened red lead [32, 33]. If the same technique could be applied on several other blackened pigments, it might lead to the development of a new restoration portable tool, in the same way Q-switched Nd:YAG laser is currently used for building stones cleaning [34–36]. Numerous advantages are associated with the use of a laser: it is intuitive and easy-to-configure, relatively cheap, and the direct control over the treated area and the use of an optical fibre make it a portable tool. Here, we address the possibility of reconverting blackened red lead and lead white on mural paintings by the use of continuous wave lasers.

Besides minium (Pb₃O₄), red lead pigment may contain lead monoxide (α-PbO, litharge and β-PbO, massicot), which is less stable, as an impurity resulting from the pigment manufacture process [5]. Due to the high colouring

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1 Reconversion is hereby used in the sense of a chemical reaction (conversion) taking place backward. Here the conversion is the oxidation to plattnerite; the reconversion is thus the formation of cerussite or hydrocerussite (white) or minium (red) from plattnerite (black) [6].
strength of minium, such impurities have little influence on the chromatic properties of the pigment [1]. Aze et al. wrote a review of red lead alteration in artwork, along with ascribed darkening mechanisms and aggravating conditions [5]. Red lead darkening originates from the transformation of minium into plattnerite (β-PbO₂) [12–14]. Such an alteration process has often been reported on fresco-like mural paintings [27–29]. No restoration method has been developed, most likely due to the complexity of the lead-oxygen system, which includes numerous crystalline varieties. Minium then massicot (β-PbO), as well as other intermediate products are formed from plattnerite at temperatures summarized in Table S-2 in the SI section [37–45]. Thermal reduction of plattnerite under a Raman laser beam, which complicated the analysis, was reported by Burgio et al. [46]. Aze et al. successfully profited from this phenomenon to achieve the thermal reconversion of blackened minium by continuous wave (CW) Ar⁺ (514 nm) and Nd:YAG (1064 nm) lasers irradiation [32].

Lead white’s main component is hydrocerussite (2PbCO₃∙Pb(OH)₂), but cerussite (PbCO₃) can be present as well, both being in chemical equilibrium [7, 47, 48]. Depending on the “stack process” [49, 50] parameters, the hydrocerussite/cerussite ratio can range from 1:2 to 3:1 [51, 52]. Lead white was used alone, or as an admixture together with calcite, gypsum, kaolin or baryte, in a variety of media such as linseed oil, gum Arabic, egg yolk, egg tempera and animal glue [2]. The blackening of lead white in mural painting is frequent and usually ascribed to its oxidation to plattnerite, which was sparingly used as a black pigment [53]. Thermal decomposition of hydrocerussite and cerussite leading to plattnerite was already studied by various authors (Tables S-3 and S-4 in the SI section summarize these studies). Tables S-5 and S-6 in the supplementary information (SI) present an exhaustive review of lead white oxidation in mural paintings [8, 9, 15, 18–26, 54–59] and in art objects [60–64]. Kotulanová et al. showed that in aqueous solution, the oxidation of lead white to plattnerite is only observed in presence of strong oxidizing agents [7]. Petushkova and Lyalkova found that H₂O₂-releasing bacteria, which developed in the animal glue-based binder, could be responsible for lead white oxidation [8]. Giovannoni et al. showed that the alkaline lime environment of a fresco mural painting lowers the Pb(IV)/Pb(II) redox potential sufficiently for the plattnerite formation to be caused by weak oxidizing agents such as hydrogen peroxide in high humidity conditions [15], which is in line with the Pourbaix diagram of lead [65]. Bernard et al. found that at pH = 8.4, the potential required to oxidize hydrocerussite to plattnerite is 0.7 V [64]; incidentally, oxidation of hydrocerussite to plattnerite at pH 8.4 in chlorinated water was reported [66]. Vagnini et al. found evidences of plattnerite formation in a secco murals, which made them question the role of chlorine [9]. And later, they showed that the alkalinity of a fresco murals is not sufficient for the oxidation to be spontaneous and thus that it requires an oxidizing agent [10]. In a nutshell, plattnerite formation from lead white seems to happen in the presence of oxidizing agents, the required strength of which being determined by the alkalinity of the painting. Besides, the composition of lead white seem to play an important role, as cerussite and hydrocerussite face different alteration patterns, the latter being more reactive [7, 10, 67]. Few methods of restoration of blackened lead white have been tested [15, 18, 25, 30, 31], but they involve chemical treatments which put the support at risks [15, 18].

Our assessment of the potentiality of using CW lasers (Nd:YAG, Ar⁺ and diode) to restore darkened red lead and lead white-containing mural paintings is hereby reported. It is grounded on a thermodynamic study of the reconversion reaction by thermogravimetric analysis (TGA) and on laser irradiation trials monitored by infrared (IR) thermography. We assessed the effectiveness of the treatment on pure plattnerite pellets, and naturally darkened mural painting samples coming from experimental ageing walls. We studied the irradiation conditions influences (laser wavelength, beam profile, irradiance, time) on the reconverted layers compositions, homogeneities and thicknesses. The latter were characterized by spectrocolorimetry, scanning electron microscopics (SEM), X-ray diffraction (XRD) and micro-Raman spectroscopy. We present here the results and discuss them within the framework of the development of a restoration tool.

2 Materials and methods

This section describes our experimental approach in the main lines; experimental details and procedures can be found in the SI section.

2.1 Study of the reconversion reactions

The first part of our study aimed at determining the parameters of the reconversion reactions following Eqs. 1, 2 and 3. Their Gibbs free energies of reaction ΔG were first calculated in order to determine in which temperature range they are thermodynamically possible. We then had to examine the thermal decomposition of plattnerite, which has been studied in air by thermogravimetric analysis (TGA) [37–45]. Table S-2 in the SI section summarizes the plattnerite → minium and minium → massicot reaction temperatures that were measured by these authors. On the other hand, the thermal decomposition of plattnerite in a CO₂ or in a CO₂/H₂O atmosphere was never studied. We thus conducted this study by TGA
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with a CO₂ flux and the reactions products were characterized by means of μ-DRX. Note that, conversely, the thermal decomposition of hydrocerussite and cerussite [41, 68–71], sometimes in a CO₂ atmosphere [72–74] have already been studied (Tables S-3 and S-4 in the SI section).

Equation 1: envisaged reaction for the reconversion of platnerite to minium

\[ 3 \text{PbO}_2 \rightarrow \text{Pb}_3\text{O}_4 + \text{O}_2 \] (1)

Equation 2: envisaged reaction for the reconversion of platnerite to cerussite

\[ \text{PbO}_2 + \text{CO}_2 \rightarrow \text{PbCO}_3 + \frac{1}{2} \text{O}_2 \] (2)

Equation 3: envisaged reaction for the reconversion of platnerite to hydrocerussite

\[ 3 \text{PbO}_2 + 2 \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{PbCO}_3 \cdot \text{Pb(OH)}_2 + \frac{3}{2} \text{O}_2 . \] (3)

2.2 Laser heating modelling

We then attempted to model the thermal response of platnerite when irradiated by a CW Nd:YAG laser. We first determined some optical and thermal parameters. Its specific heat capacity, which is temperature-dependent, was measured by differential scanning calorimetry (DSC) (Fig. S-2 in the SI section) [75]. Its reflectance at 1064 nm was measured with a UV–Visible-NIR spectrophotometer equipped with an integrating sphere (Fig. S-3 in the SI section). Other parameters were extrapolated, as explained in [76]. We then used a previously developed 3D analytical model of the laser heating of materials absorbing energy from an incident laser beam. The experimental results were properly modelled in the first times of irradiation. However, after a few seconds the model does not reproduce the laser heating, due to the lack of consideration of convection and radiation phenomena [76], which is why these results will not be further discussed here.

2.3 Laboratory laser reconversion trials

Laser irradiation trials were conducted on pure platnerite pellets as well as on naturally aged red lead-containing paint samples [77]. Figure 1 describes the experimental setup [78] we used for the laser irradiation trials: the laser beam, and the gas flux (CO₂ or CO₂/H₂O) [79] in the context of lead white reconversion, were directed toward the sample. The goal being to achieve a thermal treatment and not an ablation, the use of continuous wave lasers was preferred to that of Q-switched lasers. An IR camera was used to monitor the surface temperature evolution during laser irradiation. The influence of the laser irradiance, irradiation time, wavelength and beam profile on the reconversion were assessed. Reconverted samples areas were characterized by spectrocolorimetry, SEM–EDS and XRD. SEM, Optical microscopy and Raman were also used to study reconverted samples cross sections. Note that Raman analysis of platnerite is complicated by its sensitivity under the laser beam, which Burgio et al. and more recently Costantini et al. managed to assess [46, 80].

3 Results and discussion

3.1 Study of the reconversion reactions

Figures S-4, S-5 and S-6 in the SI section show the calculated Gibbs free energies ΔG and enthalpy ΔH of the envisaged reconversion reactions. No data were available for the platnerite to hydrocerussite reaction. We determined the temperature thresholds at which the ΔG changes sign. The reactions are thermodynamically feasible when ΔG < 0, thus in the temperature ranges summarized in Table 1. Moreover, the sign of ΔH indicates if the reactions are endothermic or exothermic in the considered temperature range. The thermal decomposition of platnerite in air was already studied by...
TGA, and the compounds were identified. The plattnerite to minium reaction occurs at 375 °C [38] and the minium to massicot reaction occurs at 552 °C [41] (see table S-2 in the SI section for other results from various authors). These results are in line with the temperature threshold that we determined. We found that annealing plattnerite at 455 °C during 6 h yields pure minium (verified by XRD, as Fig. S-7 and Table S-7 in the SI section show). To see if it is possible to form PbCO3 from plattnerite, we studied its thermal decomposition in CO2 and characterized the reaction products by µ-XRD at various temperatures (diagrams displayed in Fig. S-8 in the SI section). Figure 2 displays the resulting TGA curve and identification results. It shows first a small mass loss attributable to water desorption then a mass intake until ca. 200 °C, followed by a slight mass loss until ca. 400 °C. No chemical or structural change is detected in this temperature range by µ-XRD. Two major reactions then happen at 490 °C and 640 °C respectively (local minimum value of the first derivative of the TG signal). These correspond to mass losses of 4.36% and 6.47% respectively (local maximum value of the first derivative of the TG signal, 0.01% precision). Measured mass losses are consistent with the theoretical values that are expected for minium (4.46%) and massicot (6.69%) that have been identified by µ-XRD. No cerussite has been formed in these conditions. Basing ourselves on the calculated Gibbs free energy of reaction (Table 1), we let plattnerite in CO2 during 50 h at 250 °C, using a slower temperature ramp (5 °C min⁻¹). No mass intake or loss happened and the resulting product has been identified as plattnerite. The carbonatation of plattnerite in dry CO2 is probably kinetically so disfavoured that it is not a viable route to achieve the reconversion.

### 3.2 IR thermography

To monitor the temperature, we needed plattnerite emissivity in the measurement range of the IR camera, [7.5; 13] μm. We used the value measured by Schmidt: a 0.3 “IR emissivity” on lead dioxide coatings designed for solar panels [81]. Another source indicates a 0.28 emissivity at 258 °C in the [2.5; 50] μm range [82]. We were then able to monitor the temperature evolution during laser irradiation with the IR camera (Fig. 1). Figure 3a displays the evolution of radial temperature during laser irradiation, using a CW Gaussian shaped 1080 nm diode laser. At 1 s, the profile is quasi-Gaussian, with a ΔT dropping at 1/e of the maximum at a 1.8 mm radial distance which is close to the laser beam 1/e radius. As the irradiation goes on, the temperature variation profile gets further from a Gaussian profile, with an increasing radius at 1/e of maximum ΔT (Fig. S-9 in the SI section). This can be explained by lateral thermal diffusion happening at long irradiation times. Figure 3b shows the maximum temperature measured near the centre of the pellet. When no reconversion is observed it reaches a plateau which is higher as the laser irradiance increases. Energy can be lost by convection, radiation and diffusion, leading to the saturation that is observed. However, the broadening of the temperature profile that is observed on Fig. 3a indicates that diffusion is probably the most important phenomenon. Figure 3c shows the plateau temperature rising linearly with the laser irradiance ($r^2=0.9961$ for a linear fit). This is expected and confirms that neither the emissivity nor other optical and thermal parameters of plattnerite vary much over this temperature range. Above 152 kW m⁻², which corresponds to a plateau temperature of 375 °C, plattnerite is expected to decompose into minium, according to the reaction temperature that was measured by Clark et al. [38].

### 3.3 Laser reconversion trials

The thermal reduction of plattnerite to minium that indeed occurs in the same conditions at irradiances higher than 152 kW m⁻² is clearly noticeable under the form of a red/orange spot (Fig. 4a). Modifications of the plattnerite pellets colours occurred between 5 and 10 s of irradiation, in
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accordance with Fig. 3b. No further visual nor chemical difference is observed at higher irradiation times. Spectrocolorimetric measurements show an increase of the specular reflectance at wavelengths longer than 560 nm (Fig. 4b). This is consistent with the optical properties of plattnerite and minium (see Fig. S-10 in the SI section for the standard spectra of these compounds). The corresponding $L^*a^*b^*$ values indicate that the irradiated area turns to red with a $\Delta E$ of 34. We found a good agreement between the experimental reconversion threshold and the threshold we predicted from IR thermography measurements and Clark et al.’s results (Fig. 3c). This can be interpreted as a confirmation that the IR emissivity we measured is plausible. Above the reconversion threshold, the temperature keeps increasing without showing no plateau and then decreases slowly. Minium absorbs less than plattnerite at the laser wavelength (Fig. 3b) and would thus be less heated by the laser, which can be a possible explanation to this. Other changes in the thermal properties can also explain this observation. Moreover, the endothermicity of the reaction can also be part of the phenomenon. However, the fact that both plattnerite and minium can be present in these samples and that they have somewhat different IR emissivity (minium emissivity is 0.93 at 398 °C [82]) prevent us to discuss these IR thermography data further.

3.4 Power density threshold

The above results were obtained with a Gaussian shaped laser beam. The energy being concentrated in the inner part of the beam (Fig. 5b), the surface temperature reached during irradiation is higher when closer to the beam centre. The diameter of the reconverted minium area on Fig. 4a is 1.23 mm. It was obtained at 205 kW m$^{-2}$ with a 3.48 mm beam diameter (1/e value). According to the Gaussian distribution of power, the reconversion is thus effective at power densities higher than 181 kW m$^{-2}$.

3.5 Massicot formation at high irradiances

Using a top-hat CW Nd:YAG laser a yellow compound, later identified as massicot $\beta$-PbO, was created at irradiances higher than 2605 kW m$^2$. This is expected, since massicot is formed from minium at 552 °C [41]. The wide range between the irradiance threshold of reconversion to minium and to massicot is likely due to the fact that minium absorbs less in the infrared range than plattnerite, and is thus heated less efficiently. This can be a problem when using a Gaussian shaped laser beam, as shown by Fig. 5a: the central area has been reconverted to massicot whereas a minium ring is formed around massicot, as the micro-Raman identification show (Fig. S-11 in the SI section). In this case, the power density is so high at the centre of the beam that massicot is formed, and high enough around the centre of the beam to form minium (Fig. 5b). This phenomenon can be a problem in the context of a restauration process. Therefore, the use of a top-hat laser beam profile would be better.

3.6 Laser wavelength influence

We used an Ar$^+$ (488 nm) and a FAP-S (810 nm) laser and conducted the same reconversion trials. We observed the same processes of minium then massicot formation, although at somewhat different irradiance, summarized in Table 2. The minium reconversion threshold is higher for the Ar$^+$ than for the 1080 nm diode laser, both being
Gaussian-shaped. A higher absorbance of plattnerite at 1080 nm than at 488 nm could explain this difference. The various beam profiles make it risky to compare the other reconversion thresholds. However, we can still notice that the irradiance range in which minium is formed, before it turns to massicot, is wider in the case of the Nd:YAG laser (1064 nm) than in the case of the FSP-S diode laser (810 nm), which is itself wider than in the case of the Ar$^+$ laser (480 nm). This is explained by the considerably higher absorption of shorter wavelengths by minium than longer wavelengths. In practice, a suitable Ar$^+$ laser irradiance for plattnerite reduction into pure minium was practically unreachable. A secondary transformation into massicot was subsequently achieved through excess local heating, which makes this laser unsuitable for restoration purposes.

3.7 Naturally aged samples

Irradiation tests on darkened red lead-containing paint samples showed the same results. However, the irradiance thresholds were notably higher than those measured for pure plattnerite pellets. It is possible that such differences originate from the higher reflectivity of naturally aged paint samples. This latter is attributed to the presence of gypsum, which appeared during ageing, but also to the brown colour of finely divided plattnerite particles. It can also be attributed to differences in the surface state of the samples, in terms of rugosity or porosity. Large-scale irradiation tests were carried out at by translating the sample under the laser beam along two directions, with a mean local irradiation time of ca. 5 s. The laser irradiance (1000 kW m$^{-2}$ calculated by using the 1/e beam radius) was selected so that all plattnerite grains were transformed into minium. Such treatment produced a quasi-uniform red area (Fig. 6). The
presence of lighter stains arises from gypsum, which did not evolve during laser irradiation. Observations of the sample cross-section (Figs. 7 and S-12 in the SI section) show that the whole darkened layer has been reverted into a 50–80 µm thick red homogeneous phase. Such depth efficiency may result from the heat diffusion within the alteration layer. XRD and micro-Raman analyses of this phase confirmed the presence of minium, without any lower lead oxide in the reconverted layer (Figs. S-13 and S-14 in the SI section).

### 3.8 Lead white reconversion

Laser trials were also made on plattnerite with a CO₂ or CO₂/H₂O input. The same reactions were observed, but the gaseous flux had a cooling effect and the reconversion irradiance threshold were thus higher. No species other than minium or massicot were found. This is consistent with the TGA results, which show no carbonatation of plattnerite in CO₂ and clearly indicates that the reactions described by Eqs. 2 and 3 are not suitable reconversion routes. Minium \[83–86\] and PbO \[87, 88\] can react with H₂O and CO₂ at the solid state to form hydrocerussite or cerussite. Note that the formation of plumbonacrite, a white compound, from minium has also been evidenced \[89\]. Often, the formation

### Table 2  Minium and massicot reconversion thresholds for various lasers. Values have been calculated by using the 1/e beam radius

| Source                          | Plattnerite to minium (kW m⁻²) | Minium to massicot (kW m⁻²) |
|--------------------------------|--------------------------------|-----------------------------|
| CW Gaussian shaped diode (1080 nm) | Laser irradiance: 152          | Effective power density: 181 |
| CW top-hat Nd:YAG (1064 nm)      | 109                            | 2605                        |
| FAP-S Pb10 profile (810 nm)      | 275                            | 504                         |
| CW Gaussian shaped Ar⁺ (488 nm)  | 136                            | 151                         |

![Fig. 6](image) Darkened red lead paint sample after irradiation by a CW top-hat Nd:YAG laser (red part on the right) at 1000 kW m⁻². The lighter stains designated by an arrow are due to gypsum. Cracks were present before the treatment.

![Fig. 7](image) Backscattered electron micrographs of the paint cross-sections showed in Fig. 6 in a the original blackened area, mainly constituted by plattnerite; b the reconverted red area constituted by minium grains.
of cerussite or hydrocerussite from PbO (generally identified as massicot) is observed spontaneously in air at ambient temperature when the latter is the degradation product of lead white irradiated by a Q-switched Nd:YAG laser beam [90–95]. Hence, it could be possible to form cerussite or hydrocerussite from plattnerite via the intermediary formation of massicot and its subsequent exposition to ambient CO₂ or CO₂/H₂O. Studying the latter reaction is a first step toward the assessment of the possibility to reconvert darkened lead white by this route.

4 Conclusion

The formation of cerussite from plattnerite in CO₂, an exothermic reaction spontaneous under 320 °C was not observed during thermogravimetric analysis. Only the formation of minium (at 490 °C) massicot (at 640 °C) were observed. We monitored the temperature during laser irradiation trials by IR thermography. In air, we observed an irradiance threshold under which the temperature rises to a plateau and above which reversion to minium takes place at the expected temperature (375 °C). Plateau temperature rises linearly with irradiance, indicating that plattnerite thermal and optical parameter vary little in this temperature range. Spectrocolorimetric measurement show a reddening of the sample with a ΔE of 34, compatible with a reversion to minium. At high irradiances, the formation of massicot is also observed. Minium and massicot reversion thresholds depend on the laser wavelength. Nd:YAG minium reversion range ([109; 2605] kW m⁻² in the case of a top hat laser) is wider than AR⁺ and 810 nm diode lasers ranges. Successful trials were made on naturally darkened red led containing paint samples, moving and spending 5 s under the 1000 kW m⁻² top-hat Nd:YAG beam. XRD and micro-Raman indeed detected the presence of pure minium in reconverted layers. The reversion of plattnerite to lead white by a 1080 nm diode laser beam under gaseous flux (CO₂ or CO₂/H₂O) did not happen, in line with TGA results.

We can conclude from these results that fibered lasers are suitable to achieve the reversion of minium and massicot in mural paintings. Particularly, the top-hat Nd:YAG laser is best adapted for restauration purposes, given its broad minium reversion irradiance range and its homogeneous power density distribution. It was shown to yield good results for the treatment of a large area of a naturally aged sample, showing its suitability in restoration conditions. The direct route we assessed for lead white reversion, namely the carbonatation of plattnerite, was however unsuccessful. The formation of massicot as an intermediate product, which could later react with ambient CO₂ and H₂O to form cerussite and hydrocerussite, is a promising reversion route.

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