Laser induced yellowing of hematite $\alpha\text{-Fe}_2\text{O}_3$ based samples: a XANES and optical spectroscopy investigation

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Abstract

Nd:YAG Q-Switched (1064 nm) laser cleaning of soiled stone often results in yellower appearances than other cleaning techniques. This yellowing effect is partly due to the creation of iron-rich nanostructures through the interaction between the laser radiation and the black encrustation to be eliminated. However, the iron speciation in these newly formed compounds is still unknown. Therefore, in this paper, X-ray absorption and visible optical spectroscopies have been performed on hematite based model crust samples to (i) determine the iron speciation in the newly formed compounds and (ii) evaluate the optical properties modifications before and after laser irradiation. It was found that the yellow color is mostly linked to the presence of octahedral (O_h) Fe^{3+} ions at the surface after irradiation. A small amount of octahedral (O_h) Fe^{2+} ions is also detected, highlighting a reduction process occurring during the laser irradiation. In conclusion, the iron contribution to the yellowing of hematite crusts has been addressed.

Keywords Laser cleaning · Yellowing · Iron · XAS · Optical spectroscopy · Color

1 Introduction

Urban atmospheric pollution is responsible for the soiling of built heritage [1, 2]. In particular, the formation of black gypsum crusts in areas protected from the direct impact of rain is causing both strong aesthetic and conservation issues [3]. The removal of these undesired encrustations can be performed using various cleaning techniques such as micro-sandblasting, chemical poultices or laser [4, 5]. Laser cleaning boomed in the 1990s and is now a widely used technique thanks to its unique properties including high controllability and material selectivity [6, 7]. However Nd:YAG QS (1064 nm) laser cleaning of soiled stone sometimes results in yellower appearances than other cleaning techniques [8, 9]. This laser side-effect known as

the *yellowing effect* has raised a strong aesthetic debate, especially in France where the yellow hue was and is still considered as unsightly and undesirable [10, 11].

To quantify the yellowing process, several colorimetric studies have been performed [11–13]. They reveal that the yellower hue observed on the naked eye systematically corresponds to higher (+4 to +30) chromatic coordinate b^* values than those of (i) unsoiled areas or (ii) areas cleaned by other techniques.

Concerning the origin(s) of the yellowing effect, many studies conducted since the 1990s have shown that it is a complex entanglement of several phenomena [14]. The yellowing is often due to the unveiling of yellow layers—epigenic gypsum, oxalates, ancient treatments—located beneath the encrustation [15]. Furthermore, it is also

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linked to the creation of new-formed compounds through the interaction between the laser radiation and the black encrustation to be eliminated [16, 17].

As the black crusts chemical composition is particularly complex, the vast majority of studies concerning the new-formed compounds have been conducted using simplified model black crusts applied on pure plaster or marble substrates. These model crusts were elaborated by mixing synthetic gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and 1064 nm absorbing compounds present in black crusts, mainly iron oxides (hematite $\alpha\text{-(Fe}^{3+})_2\text{O}_3$) or carbonaceous compounds (graphite, lamp black) in various proportions [18–20]. Some recent studies have also used real black crust or dust deposits crushed into powder and mixed with synthetic gypsum to make model crust samples closer to reality [21, 22]. The different crust samples were then irradiated by a Nd:YAG QS laser (1064 nm) in standard cleaning conditions, all leading to a yellow appearance after the treatment.

In the cases of model crusts including hematite or real black crust powder [18, 20, 23] iron-rich nanostructures (≈ 100 nm) have been evidenced at the surface after irradiation using electron microscopies examination. In particular, transmission electron microscopy (TEM) analysis of irradiated hematite model crusts has demonstrated that the neo-formed compounds are crystallized nanostructures, mostly containing iron and oxygen, often along with calcium and sulphur [24]. However, the iron speciation and environment in these nanostructures have not been studied yet. Figuring out the structural properties of these iron-rich compounds will allow understanding the physical processes underlying the production of the yellow color.

2 Research aims

The present study aims at determining (i) the iron speciation and environment in the iron-rich nanostructures and (ii) the optical properties (including the color) modifications before and after laser irradiation for hematite model crusts samples.

As the iron containing compounds are nano-sized and present in very low amounts after laser irradiation, X-ray absorption near edge spectroscopy (XANES) at the Fe K edge and optical spectroscopy are two complementary and well-suited techniques which will be used to address those questions in order to determine the physical origin(s) of the yellowing process.

3 Materials and methods

3.1 Model crust preparation

Two model crusts samples containing respectively 1 wt% and 30 wt% of hematite $\alpha\text{-Fe}_2\text{O}_3$ (ALDRICH 99%) were

elaborated (respectively named H1 and H30). Indeed, 1 wt% is the order of magnitude of the iron amount naturally present in a black crust [25–27]. In addition, a model crust enriched in hematite (30 wt%) was elaborated to generate a bigger amount of iron containing compounds of interest.

Three white gypsum plates were first synthesized by hydration of a powder of pure calcium sulfate hemihydrate (ALDRICH 97%) in distilled water (50:50 wt%). Two dry mixtures composed of the same calcium sulfate hemihydrate and hematite powder (99:1 and 70:30 wt%) were then gently rubbed with a gloved finger onto the dry surface of the gypsum plates, forming a very thin soiling layer (less than 20 μm). The whole was water sprayed, inducing the formation of smooth and semi-indurated gypsum crusts. The two samples H1 and H30 were left to dry for 24 h before being irradiated by a Nd:YAG Q-switched laser device from Thomson BM Industries. The last white gypsum plate was left unsoiled and used as a reference (“unsoiled sample”) for optical spectroscopy measurements.

The laser, operating at a wavelength of 1064 nm, produced discrete pulses of laser energy up to 0.4 J with a pulse length of 15 ns. The pulse was delivered using an articulated mirrored arm and a hand-piece equipped with a 70 cm focal length convergent lens. The fluences used were 0.3–0.9 J cm^{-2} for the model crust H1 (1 wt% of hematite) and 0.2–0.9 J cm^{-2} for the enriched one H30 (30 wt% of hematite). The pulse frequency was 10 Hz. The samples were irradiated at a rate of about 0.5 min per cm^2 for H1 and 3 min per cm^2 for H30, meaning that about 300 and 1800 pulses are respectively used to clean the samples. The surface of both samples was sprayed with water prior to irradiation.

3.2 Optical spectroscopy and color measurement

Diffuse reflectance measurements were performed using an Agilent Cary 5000 spectrometer equipped with an integrating sphere coated with a polytetrafluoroethylene (PTFE) film. A white standard (Spectralon disk from Labsphere) was analyzed before each acquisition. Diffuse reflectance spectra $R(\lambda)$ were recorded in the range 250–800 nm with a spectral resolution of 1 nm.

To study the absorption bands, the apparent absorbance spectra $A_{\text{app}}(\lambda)$ were calculated using the Beer–Lambert law (extended to thick objects):

$$A_{\text{app}}(\lambda) = \log \left(\frac{I_0}{I} \right) = -\log R(\lambda) \quad (1)$$

with I_0 the initial light intensity and I the light intensity after it has go through a layer of an absorbing material characterized by an absorbing coefficient A [28]. It is

important to keep in mind that the apparent absorbance spectra $A_{app}(\lambda)$ obtained with diffuse reflectance spectroscopy data are not real absorption spectra because diffusive effects are also affecting the curves (especially if the studied material size is smaller than the source wavelength). Nevertheless, these types of spectra represent a very useful approximation and have often been used to identify the characteristic absorption bands of minerals [29, 30]. If the absorption bands are broad, which makes their attribution difficult, it is interesting to study the derivative function (first or second) in order to exacerbate the spectra subtle inflections [31]. This method called “derivative spectroscopy” has been widely used to identify iron oxides (hematite and goethite) in soils [32–34] or more recently in soiling dust materials [21]. In the present study, the derivative spectroscopy method was used using the following procedure: (i) calculation of the apparent absorbance $A_{app}(\lambda)$, (ii) Savitzky-Golay smoothing of the curve (iii) numerical calculation of the second derivative. The software Origin64 was used for all these data treatment.

Reflectance of some pure iron oxides (hydroxide) powders including hematite and goethite (ALDRICH 97%) applied on white gypsum plates has also been measured to compare their spectral signature with those of analyzed samples.

Reflectance spectra in the visible region have been treated to calculate the chromatic coordinates and thus characterize the color variations. In the present study, the CIE-LAB system was used and the coordinates L^* (brightness), a^* (green–red), b^* (blue–yellow), C^* (saturation or color purity) and h^* (hue) were calculated thanks to a program internally developed at the CRCC laboratory. The coordinates C^* and h^* are deduced from a^* and b^* using the following equations:

$$C = \sqrt{a^{*2} + b^{*2}} \quad (2)$$

$$h^* = \left(\tan^{-1} \frac{b^*}{a^*} \right) \times \frac{180}{\pi} \quad (3)$$

The RGB values were also calculated using the same program, allowing a visualization of the color on the screen.

3.3 XANES data collection and analysis

X-ray absorption near edge spectroscopy (XANES) measurements were undertaken on the beamline DiffAbs at the Soleil synchrotron (France, 2.8 GeV, 430 Ma). The used monochromator was a double crystals Si(111) with a resolution of 0.5 eV at the iron K edge. XANES spectra were recorded in fluorescence mode with a four-element silicon drift detector (SDD, Vortex-ME4[®], Hitachi) positioned at 90° to the X-ray incident beam. The flat samples were placed at 45° to the beam. The beam size

was about 300 μm $\times$ 245 μm (length $\times$ height) at 7.2 keV. XANES spectra were acquired between 7.05 and 7.35 keV on regions of interest. The energy steps was 0.5 eV near the pre-edge and the absorption edge (7105–7200 eV) and 1–2 eV before the pre-edge and after the edge. Two spectra were recorded and merged for each point of interest. The energy was calibrated with a pure iron foil whose first inflexion point of XANES spectrum is theoretically located at 7112 eV. Pure hematite and goethite applied on gypsum plates (same samples as the ones used for optical spectroscopy) were also analyzed and used as references.

The spectra were averaged and normalized using the ATHENA software from the Demeter0.9.24 package [35]. Concerning the pre-edges areas (7100–7125 eV), the background was first removed using a spline function (15 points) with the Fityk software. The pre-edges position and intensity were then determined using the integration tool of Origin64 software. This methodology relevance was ensured by placing our experimental points into the references diagram built by Wilke et al. [36] and checking that our references and the ones of Wilke et al. were matching.

4 Results

4.1 Color and optical spectra

Before the laser irradiation, the samples show either a light pink color (H1) or a wine red color (H30). After irradiation, both crusts are ablated and the substrates shift to a yellow color, visually brighter for H30 than for H1 (Fig. 1).

Taken the initial color of the samples as reference, the chromatic coordinates indicate that the yellowing is due to a combined increase of brightness L^* ($+4 < \Delta L < +47$), saturation C^* ($\Delta C^* \sim +6$) and hue h^* ($+43 < \Delta h^* < +48$)

Fig. 1 Model crusts before and after laser irradiation (top view pictures)

Table 1 Chromatic coordinates of model crusts before and after laser irradiation

Sample	Laser	L^*	a^*	b^*	C^*	h^*	RGB
Unsoiled sample	/	98.2	0.35	0.92	1.0	69.1	
H1	Before	82.9	7.2	6.2	9.5	40.8	
	After	87.3	0.13	14.9	14.9	89.5	
H30	Before	39.9	24.3	16.7	29.4	34.4	
	After	86.6	6.9	34.2	34.9	78.6

Fig. 2 Chromatic variations of model crusts before and after laser irradiation (H1 and H30); **a** polar scattergram; **b** brightness L^* as a function of saturation C^* . Legend: red circle=before irradiation; yellow square=after irradiation; black star=unsoiled sample; NB: $h^*=0^\circ$ corresponds to pure red hue; $h^*=90^\circ$ corresponds to pure yellow hue

values towards pure yellow tonality ($h^*_{\text{yellow}} = 90^\circ$) (Table 1). The polar scattergram displayed on Fig. 2 (left) allows to easily visualize the hue h^* variations. Besides, representation of brightness L^* as a function of saturation C^* (Fig. 2, right) clearly evidences the increase of saturation for both samples. It also reveals that brightness L^* increases more for H30 than for H1 which is already very bright before irradiation.

b^* values strongly increase during irradiation, reflecting the *yellowing* process ($+8 < \Delta b^* < +18$). The brighter yellow color observed for H30 is linked to a value of $b^* = +34.2$ much higher than that of H1 ($b^* = +14.9$). It is worth noting that this difference in b^* values is essentially linked to a higher saturation value C^* and neither to brightness L^* which shows similar values in both cases, nor to hue h^* which is even slightly yellower for H1 than for H30.

If we take the unsoiled sample color as a reference, we see that the C^* and b^* values are higher for the irradiated substrates than for the white plaster of a few tens of units ($+15 < \Delta b^*, C^* < +33$). The brightness values are lower as the white substrate is already very bright ($\Delta L^* \sim -10$) and the hues values are increasing towards pure yellow tonality ($+10 < \Delta h^* < +20$).

yellow square=after irradiation; black star=unsoiled sample; NB: $h^*=0^\circ$ corresponds to pure red hue; $h^*=90^\circ$ corresponds to pure yellow hue

Fig. 3 H30 reflectance spectra before and after irradiation

The reflectance spectra from which the chromatic coordinates have been calculated are displayed on Fig. 3 for the H30 sample. Before irradiation, the reflectance spectrum is similar to the one of pure hematite. After irradiation a broad absorption edge is observed. Short wavelengths are less reflected than longer wavelengths, indicating

a spectrum typical of yellow tonalities. For H1 the same type of spectrum is obtained (not shown here), but slightly attenuated by the strong reflection of gypsum.

Apparent absorbance and second derivative curves are displayed on Fig. 4 for H30 sample before (left) and after (right) irradiation. Each absorption maxima coincide to a minimum on the second derivative spectrum. Before irradiation, the second derivative shows three minima at 561, 655 and 845 nm. The minima at 561 nm correspond to a steep absorption edge whose attribution is still unclear. According to Sherman and Waite [29] the three minima correspond to three iron Fe^{3+} crystal field transitions in octahedral symmetry, the one at 561 nm being intensified by magnetic coupling between adjacent iron atoms: ${}^6A_1 + {}^6A_1 \rightarrow {}^4T_1(G) + {}^4T_1(G)$, ${}^6A_1 \rightarrow {}^4T_2(4G)$ et ${}^6A_1 \rightarrow {}^4T_1(4G)$. Other authors suggest that the first [37] or the two firsts [38] minima are due to charge transfer transitions between iron 3d and oxygen 2p orbitals $2p(\text{O}^{2-}) \rightarrow 3d(\text{Fe}^{3+})$. For the H1 sample which contains less hematite, only two minima at 560 and 850 nm are detected.

After irradiation, the shape of the curves drastically changes. The steep absorption edge shifts towards shorter wavelengths in the near UV region and can be attributed to a O–Fe charge transfer transition with an absorption tail spreading in the visible region [39]. In addition, four minima are observed at 424, 482, 560 and 990 nm. The two first bands at 424 nm and 482 nm are characteristic of iron Fe^{3+} in octahedral symmetry and can be assigned to the transition ${}^6A_1 \rightarrow 4E, {}^4A_1$ and ${}^6A_1 + {}^6A_1 \rightarrow {}^4T_1(G) + {}^4T_1(G)$ [30]. The minimum at 560 nm is probably linked to the presence of hematite residues after irradiation. The small amplitude band observed around 1000 nm can be assigned either to the transition

${}^4A_1 \rightarrow {}^4T_1(4G)$ of Fe^{3+} ion in octahedral geometry or to the transition $5T_2 \rightarrow E$ of Fe^{2+} ion, also in octahedral symmetry [30].

4.2 XANES investigation

XANES results are similar for H1 and H30 samples. Before irradiation, a spectrum characteristic of pure hematite showing a typical spiked structure near 7133.9 eV is observed (Fig. 5). After irradiation, the shape of the pre-edge, edge and post-edge oscillations has changed. Indeed, the edge is rounder and the spiked structure observed around 7133.5 eV has disappeared. The new features appear comparable to those of iron oxyhydroxides such as goethite $\alpha\text{-(Fe}^{3+}\text{)OOH}$. These modifications mean that (i) iron is still present on the surface but in a different form and (ii) chemical and structural transformations have taken place during the cleaning (Table 2).

The edge position has decreased of 0.5 eV, potentially indicating a slight reduction of iron atoms from Fe^{3+} to Fe^{2+} . As the energy shift is very small (equal to the spectral resolution), the positions of the pre-edges—which are more sensible to oxidation degree were further investigated on several zones.

Before irradiation, the pre-edges position corresponds to that of hematite at 7114.5 eV. After irradiation, a shift of 0.5 eV towards lower energies is observed (Fig. 6) for both samples (H1 and H30) and for all the investigated areas (5). Therefore, it is likely that a part of the Fe^{3+} ions is effectively reduced in Fe^{2+} . Pre-edges intensities are comparable before and after irradiation indicating that the general symmetry has not changed during laser treatment and is still mostly octahedral.

Fig. 4 H30 sample absorption and second derivative spectra before and after irradiation

Fig. 5 XANES absorption spectra at the iron K edge of H1 before and after laser irradiation; an offset has been applied to increase the readability of the figure

Table 2 Positions of the fine structures observed on the XANES spectra of H1 sample before and after laser irradiation

Sample	Pre-edge	Edge (E_0)	Top of the edge	Spiked structure	Post-edge shoulder	Post-edge oscillation
Before irradiation	7114.5	7125.1	7130.0	7133.5	7147.9	7177.0
After irradiation	7114.0	7124.6	7131.5	–	7149.0	7176.5
Hematite (ref)	7114.6	7125.5	7130.5	7133.9	7148.1	7178.0
Goethite (ref)	7114.5	7125.0	7130.5	–	7148.0	7176.8

Fig. 6 Pre-edges before and after laser irradiation for H1 and H30 samples; an offset has been applied to increase the readability of the figure

5 Discussion

The yellowing process of hematite model crusts is linked to a b^* value increase of respectively +8 and +18 units (or +15 and +33 if we take the unsoiled sample

as reference) for H1 and H30, reflecting a more intense yellowing for H30. These values are in the same order of magnitude as what is obtained in literature for hematite model crusts [18, 20]. The fact that the yellowing is more intense for H30 than for H1 indicates that the color change is probably linked to the transformation of hematite into some new-formed compounds during irradiation. This is in line with the fact that if we irradiate the unsoiled sample in the same conditions, no yellowing is observed.

De Oliveira et al. [21] recently studied dust deposits containing hematite and goethite particles. An optical spectrum very close to the one of goethite was obtained before and after laser irradiation. The authors thus suggest that the yellow appearance obtained after irradiation is linked to the presence of one or several iron-containing phase(s) having the same spectral signature as goethite. However, they cannot be more precise as different iron minerals may have comparable optical spectra.

In the present study, it was found that the iron present after irradiation is mainly in the form of Fe^{3+} ions in octahedral configuration. In addition, XANES analysis of the yellow surface reveals a different spectrum from the one of goethite, indicating that a different octahedral Fe^{3+} phase (or

several ones) is probably present. Here it is crucial to recall the fact that after irradiation iron is present in nano-sized compounds as it was revealed by the authors in a recent study [24]. The nanostructures are crystallized and have variable chemical compositions mainly including oxygen and iron (and sometimes calcium and sulphur in lower amounts). As the XANES analysis is probing a submillimeter-sized volume of matter, the spectra obtained on each point give iron speciation and environment information for all the nanostructures included in the volume probed. Therefore, on average, the different nanostructures are mostly octahedral Fe^{3+} compounds. This is quite plausible as most of the minerals containing Fe^{3+} in octahedral configuration have yellow tonalities, including iron oxy-(hydroxi)-des such as goethite $\alpha\text{-FeOOH}$ but also lepidocrocite $\gamma\text{-FeOOH}$, ferrihydrite, maghemite $\gamma\text{-Fe}_2\text{O}_3$, oxyhydroxisulfates such as schwertmannite $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)_n\text{H}_2\text{O}$ [40], iron sulfates [41] etc. For these minerals, the yellow color is produced by d-d magnetically enhanced electronic transitions plus O-Fe charge transfer [30]. In our case, the same mechanisms are thus probably responsible for the yellow color obtained after irradiation.

In addition to the $\text{Fe}^{3+} \text{O}_h$ ions, some $\text{Fe}^{2+} \text{O}_h$ ions have also been detected after irradiation. This result is consistent with the recent identification of some magnetite ($\text{Fe}^{2+})(\text{Fe}^{3+})_2\text{O}_4$ nanoparticles on the irradiated surface using ELNES spectroscopy [24].

The present study outcomes are in line with those of a Mossbauer study conducted by Gracia et al. [42] showing that magnetite plus an unidentified Fe^{3+} compound were created after laser irradiation of mixtures of hematite and gypsum powders at 0.7 J cm^{-2} (30 Hz) during 16 min. It is worth noticing that the powdered mixtures used in the study (stored in petri boxes) do not appear yellow after irradiation but rather grey. Besides, De Oliveira et al. [20] has also shown that depending of the fluence and hematite concentration, a blackening rather than a yellowing can be obtained after laser irradiation of hematite model crusts. These results are thus questioning the importance of laser irradiation parameters and likely of the presence of a white substrate beneath the encrustation to the yellowing process. In particular, as magnetite appears black at the macro and micro scale how can its presence contribute to the yellowing? An optical modeling of a white substrate covered by dispersed magnetite nanoparticles has revealed that the whole system can appear ochre beige, proving that the presence of nanoparticles of magnetite after irradiation may also contribute to a yellow appearance [43].

6 Conclusion and perspectives

This study focuses on the iron contribution to the yellowing process of hematite based samples, elaborated to simulate stonework covered by pollution encrustations. Our results reveal that the laser yellowing of hematite crusts is due to the presence of iron at the surface after irradiation, essentially in the form of $\text{Fe}^{3+} \text{O}_h$, which is the configuration of most of the yellow iron containing minerals. A low amount of $\text{Fe}^{2+} \text{O}_h$ is also present, consistent with the identification of magnetite Fe_3O_4 nanoparticles in a previous study.

Furthermore, the complementary use of XANES and optical spectroscopies has proved to be efficient to determine the iron speciation and environment for model crusts samples. It would now be useful to undertake a similar investigation on real soiled stone samples, before and after laser cleaning.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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