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Effect of analytical proton beam irradiation on lead-white pigments, characterized by EPR spectroscopy

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ABSTRACT

Analytical techniques using proton beams with energy in the MeV range are commonly used to study archeological artefact and artistic objects. However ion beams can induce alteration of fragile materials, which is notably the case of easel paintings, limiting the use of these techniques. We used continuous wave EPR and pulse EPR spectroscopy to reveal the effect of 3 MeV proton irradiation on lead carbonates, which were extensively employed as white pigments from the antiquity to the 20th century. Two kinds of paramagnetic centers were identified in cerussite ($PbCO_3$): the first one is CO_3^- radicals formed by hole trapping by CO_3^{2-} ions, and the second one is NO_3^{2-} radical resulting from electron trapping by NO_3^- impurities. Hydrocerussite ($2PbCO_3{\cdot}Pb(OH)_2$) is the most darkened material under proton beam, however it exhibits no NO_3^{2-} radicals and 20 times less CO_3^- radicals than cerussite. Consequently these paramagnetic centers are not directly responsible for the darkening of lead-white pigments. We proposed that their higher instability in hydrocerussite might be at the origin of the formation of color centers in this material.

1. Introduction

Because cultural heritage artefacts are precious and often unique, non-destructive analytical techniques are preferred for the characterization of their constituting materials. Among the different available techniques, methods based upon bombardment with MeV ion beams produced by small particle accelerators have gained considerable interest, as attested by the numerous applications to art and archaeology [1,2]. The reason is that the combination of Particle induced X-ray emission (PIXE), Rutherford backscattering (RBS) and Nuclear reaction analysis (NRA), can provide a thorough and accurate characterization of the artefact materials without requiring sampling. The purported non-damaging character of ion-beam analysis techniques is however questioned when analysing sensitive and fragile artefacts in which impinging ions can induce modifications [3,4]. Pigments and binders present in paintworks are among such fragile materials, and consequently the risk of damage has hampered the development and the routine application of ion beam analysis [5]. An important problem in paintings is the damage induced in lead-white, the pigment most employed by artists till the 20th century. This material is a mixture of lead carbonate (cerussite $PbCO_3$) and basic lead carbonate (hydrocerussite $2PbCO_3{\cdot}Pb(OH)_2$) in variable proportion. This white powder can undergo dramatic modifications under the probing proton beam, ranging from reversible dark stains to irreversible degradation depending on the ion fluence [6–9]. Visual modification of hydrocerussite have shown to occur above a 2.5 μC/cm^2 of 3-MeV protons (1.6×10^{13} protons/cm^2), and above these values for cerussite which is more resistant than hydrocerussite. The identification of radiation-induced defects and the understanding of the involved processes is mandatory for a routine ion-beam analysis of paintworks, and more generally for the development of damage mitigation strategies when analysing cultural heritage materials with ion beams. In this work, Electron Paramagnetic Resonance (EPR) was used to investigate the effect of proton beam irradiation in cerussite and hydrocerussite.

2. Sample synthesis, irradiation and characterization

Pure cerussite $PbCO_3$ and hydrocerussite $2PbCO_3{\cdot}Pb(OH)_2$ powders were prepared by co-precipitation of stoichiometric proportions of $Pb(NO_3)_2$ and Na_2CO_3 (Merck, 99%). These materials were synthesized under controlled pH by adding a solution of NaOH (Normapur, granules, 100%). Cerussite was obtained at pH < 6 and hydrocerussite at

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$8 \leq pH \leq 10$. The samples were pressed at 8 tons in 8-mm pellets of 1 mm thickness. Cerussite is orthorhombic (aragonite structure) with space group *Pmcn*. Hydrocerussite is rhomboedric (space group $R3\overline{m}$) and is described by a succession of BAABAA layers, with A layer containing Pb atoms and CO_3 groups, while B layer is composed Pb atoms and OH groups [10]. Bilayers AA correspond to cerussite. The powders were characterized by X-ray diffraction (XRD) using a Panalytical X'Pert Pro (45 kV, 40 mA, CuK_α) = 0.15405 nm, combined with Rietveld refinement. The synthesized samples were found to be pure cerussite and pure hydrocerussite phases within the precision of XRD. Purity of phases was also checked by their photoluminescence (PL) properties (see Supplementary Fig. S1) [11]. In association with XRD, Raman spectroscopy was used to detect eventual structural changes induced by proton-beam irradiation. Raman spectra were recorded at room temperature on a Renishaw Invia micro-Raman spectrometer equipped with a CCD detector. The 532 nm line of a frequency doubled Nd:YAG laser was used for the excitation.

Cerussite and hydrocerussite powder pellets were irradiated at AGLAE accelerator (Palais du Louvre, Paris) by 3-MeV protons with a fluence of 14 μC/cm^2 (8.75×10^{13} protons/cm^2). This fluence corresponds to a normal value for ion-beam analysis of cultural heritage materials (irradiation of 1-mm^2 beam of 1 nA during 140 s). The beam was raster-scanned over a large area of the pellet (5 mm × 5 mm) to produce irradiated zones that are large enough for EPR measurements, hence the shape of the dark marks in Fig. 1. After irradiation, the shallow irradiated layer was removed from the pellet and introduced in quartz tubes for EPR analysis. Thus the studied powder contained the irradiated (coloured) material with an uncontrolled proportion of non-irradiated (colourless) material.

Continuous wave EPR spectra (CW-EPR) were recorded at X-band (≈9.4 GHz) and Q-band (≈34 GHz) using a Bruker ELEXSYS E500 spectrometer equipped with 4122SHQE/011 and ER5106QTE resonators, respectively. The spectra were recorded at room temperature and at 34 K by using an ESR300 helium flow cryostat from Oxford Instruments. Pulsed-EPR experiments were carried out at 5 K with a Bruker ELEXSYS E500 X-band spectrometer equipped with a Bruker cryostat "cryofree" system. Echo-detected EPR spectra (EDEPR) were recorded using standard Hahn echo (π/2-τ-π-τ-echo sequence) with π/2 and π pulse duration of 16 and 32 ns, respectively. The angles π/2 and π represent the flip angles of the electron magnetization. The EDEPR represents the intensity of the spin echo versus the magnetic field strength. Hyperfine Sublevel Correlation spectroscopy (HYSCORE) was used to reveal hyperfine interactions with ^{207}Pb ($I = 1/2$; 22.1% abundance), ^{13}C ($I = 1/2$; 1.1% abundance) and ^{1}H nuclei ($I = 1/2$; 100% abundance). In this technique, a spin echo is generated by the pulse sequence π/2-τ-π/2-t_1-π-t_2-π/2-τ-echo. Its intensity is measured upon varying stepwise the times t_1 and t_2 at constant time τ. The length of the π/2 pulse was fixed at 16 ns, and the length of the π pulse was optimized (40 ns) using nutation experiments for optimum echo inversion. The τ value was optimized by performing a stimulated echo experiment (π/2-τ-π/2-T-π/2-τ-echo sequence) at different τ values from 108 to 300 ns. To avoid blind spot effect for all nuclei, an optimum τ of 164 ns was used. For HYSCORE, 256 × 256 data points were collected for both t_1 and t_2 with increments of 28 ns. The unmodulated part of the echo was removed by using a second-order polynomial background subtraction. The magnitude spectrum was obtained after a 2D Fourier transform of the spectra by using Hamming apodization function. The EPR spectra were simulated with Easyspin software [12].

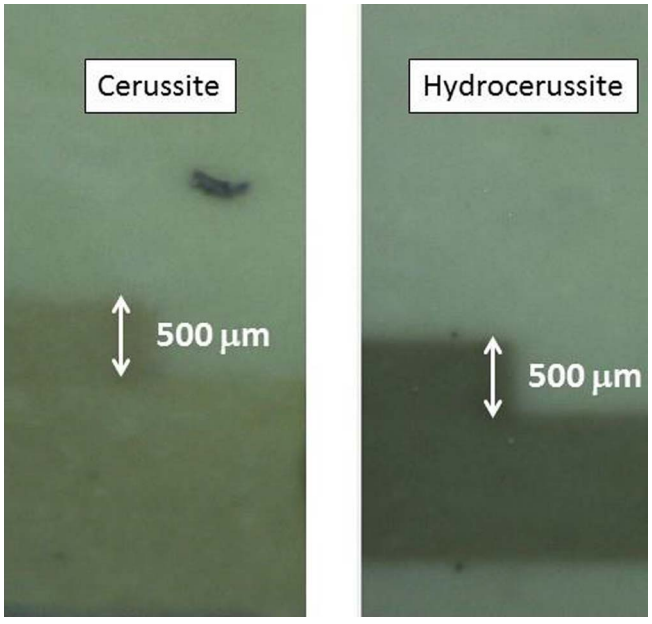

Fig. 1. Optical image of cerussite and hydrocerussite. The darkened zones are produced by 3-MeV proton irradiation.

3. Results

The visual effect of proton beam irradiation on cerussite and hydrocerussite is shown on Fig. 1, where the dark areas correspond to irradiated zones [7–9]. The darkening appears much more pronounced in hydrocerussite (brownish) than in cerussite (yellow). With the beam fluence used in this work, proton irradiation does not modify the XRD pattern of the compounds (Supplementary Fig. S2), as previously shown by Absil et al. [7]. This lack of structural modification under moderate proton beam fluence is confirmed by Raman spectroscopy. The variation of the Raman band corresponding to the symmetrical CO stretching mode [13] is shown in Supplementary Fig. S3. The laser beam was focussed on the irradiated zone (interrupted lines) and the unirradiated zone (full line). No variation of Raman shift and Raman shape were observed after proton irradiation except a small decrease of intensity. This weakening of Raman intensity might be due to the darkening of the irradiated area, which partially absorbs the incident light and decreases the diffused light intensity. Consequently there is no evident structural change induced by proton irradiation, at least with the beam fluence used in this work. The structural modifications observed by Beck et al. [9] by Raman and XPS spectroscopy most probably resulted from the higher irradiation doses used in their experiments.

3.1. Continuous wave EPR

After irradiation, the room temperature EPR spectrum at X-band of cerussite exhibits more than five lines (top of Fig. 2) due to the combined effect of the hyperfine (hf) interaction and the *g*-anisotropy of one or several paramagnetic defects. These lines are absent before irradiation. In order to disentangle this complex spectrum, EPR spectrum of cerussite was also recorded at Q-band (bottom of Fig. 2). At this higher frequency, the effect of *g*-anisotropy is enhanced without affecting the hf interaction. A triplet of lines with equal intensities is clearly observed around 1220 mT, showing that the unpaired electron of the paramagnetic center is interacting with an element possessing a 100% abundant isotope with nuclear spin $I = 1$, giving $2I + 1 = 3$ hf lines. Such element is not naturally present in pure $PbCO_3$ as the only magnetic isotopes ^{207}Pb and ^{13}C are characterized by $I = 1/2$ and a low abundance (22.1% and 1.1%, respectively). The isotope with $I = 1$ that can be potentially present in cerussite is ^{14}N (abundance 99.3%), as Pb $(NO_3)_2$ was used for the Pb source in the synthesis. The signal is thus ascribed to NO_3^{2-} radical with spin $S = 1/2$ resulting from the trapping of an electron by NO_3^- impurities. The three prominent EPR lines correspond to NO_3^{2-} radicals with their symmetry axis oriented perpendicularly to the external magnetic field, while the weak lines in the range 1225–1245 mT (Fig. 2) correspond to NO_3^{2-} radicals with their symmetry axis parallel to the external magnetic field. However the