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Damage induced by proton irradiation in carbonate based natural painting pigments

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Abstract

The so called "dark spot" phenomenon produced during proton irradiation of pigments is an important factor to determine experimental conditions of ion beam analysis of pigments in paintings, miniatures, pottery and other art objects. Recently it has been suggested that this phenomenon could be due to the formation of colour centres during irradiation, but there is scarce knowledge about the characteristics and the reversibility of the damage.

In this work a representative set of natural carbonate minerals, traditionally used as pigments, were exposed to proton irradiation in an external beam set-up, in order to simulate routine external proton induced X-ray emission (PIXE) analysis conditions of an art object. During irradiation ionoluminescence (IL) combined with PIXE were employed to identify the microscopic processes involved in the proton damage. After irradiation, two well-established techniques for the study of colour centres, thermoluminescence (TL) and optical absorption were used. Particularly, TL is a very sensitive technique to detect very low concentrations of radiation induced defects.

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1. Introduction

Although PIXE analysis of paintings has been developed during the last few decades for the study of art and archaeological objects, including important examples of paintings, there are scarce studies concerning possible damage on natural pigments and other art materials. Two recent works pay attention to the damage induced by proton irradiation in pigments [1] and ceramics [2]. Both reveal the apparition of "dark spots" during proton irradiation associated with a carbonate based composition and, to some extent, with colour centres.

The main objective of this work is to better understand the physical–chemical mechanisms

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responsible for the radiation-induced damage and the "dark spot" phenomenon. For this purpose a representative set of natural carbonate minerals, that is, calcite, dolomite, cerusite, malachite and azurite, traditionally used as pigments [3], were irradiated in an external beam set-up, in order to simulate routine external PIXE analysis conditions of an art object. Several analytical techniques, namely PIXE, ionoluminescence (IL), thermoluminescence (TL) and optical absorption were employed to get information about composition of the samples and about the colour centre formation. Both IL and TL are particularly sensitive techniques to the first stages of radiation damage.

2. Samples and experimental techniques

Five different carbonate samples, from several structural types, including rhombohedral (calcite and dolomite), orthorhombic (cerusite) and monoclinic (malachite and azurite), traditionally used as pigments, were selected for this study. All the minerals used in the present work were previously characterised by X-ray powder diffraction (XRD), and by atomic absorption spectrometry (AAS) [4].

The samples were prepared as follows by using a standard TL sample preparation method. After having been hand-crushed in an agate mortar a suspension in acetone was prepared with the powder which, after evaporation, left a 50 μm grain size deposit on a steel disc. Only two samples were specifically prepared for optical absorption by cutting and polishing the bulk mineral.

The irradiation of the samples and the simultaneous PIXE and IL experiments were carried out with 3 MeV protons at the new external microbeam installed at the 15° extension line at the 5 MV Tandetron accelerator at the Centro de Microanálisis de Materiales (CMAM) in Madrid [5,6]. In order to simulate standard external micro-PIXE analysis conditions, the samples were placed at 3 mm from the exit window and were irradiated in nine different points with a 100 μm beam diameter and 130 nA beam current during 120 s at each point. The light emitted from the samples was directly collected via a 800 μm diameter optic fibre to an optical multichannel analyser (OMA). After a preset integration time (that can be chosen in the range 1–10 s), the IL spectra, in the range of 190–850 nm, was read out by a computer.

TL experiments were undertaken using a DA-10TL system developed by RISO National Laboratory, in which the integrated light signal is detected by a photomultiplier tube as the sample is heated to 500 °C with a heating rate of 5 °C/s in a N_2 atmosphere.

The two bulk samples, prepared for optical absorption (calcite and cerusite), were irradiated at only one point with a 0.5 mm beam diameter and 18 nA beam current for about 30 min in order to obtain a detectable optical absorption signal. Optical absorption measurements, were performed with a spectrophotometer Hitachi u-2000 at room temperature.

3. Experimental results and discussion

3.1. Ionoluminescence and PIXE

The IL spectra of the two rhombohedral carbonates (calcite and dolomite) are shown in Fig. 1. As seen from the figure, the main emission consists of a broad band with peak wavelengths at 600 nm for calcite and at 640 nm for dolomite. Comparing these results with the energy level diagram for Mn^{2+} in calcite and dolomite [7], the light emissions can be assigned to the transition $^4T_{1g}$–^6S. This result is in accordance with the presence of Mn in the sample that had been detected by PIXE and is also in good agreement with previous photoluminescence and ionoluminescence analysis [4,8,9]. Therefore, the important role played by Mn as a recombination centre in calcite and dolomite has been confirmed.

Also in Fig. 1 the IL spectrum of the cerusite is shown. It consists of a broad band with peak wavelength at 500 nm, that has been associated with the inverse $^3T_{1u}$–$^1A_{1g}$ transition of Pb^{2+} ions placed in Oh symmetry [7]. This result is consistent with the intense yield of Pb found by PIXE analysis and reveals that, in this case, Pb is the relevant impurity as a recombination centre for light emission.

Unfortunately no IL emission was detected in malachite and azurite, but based in previous

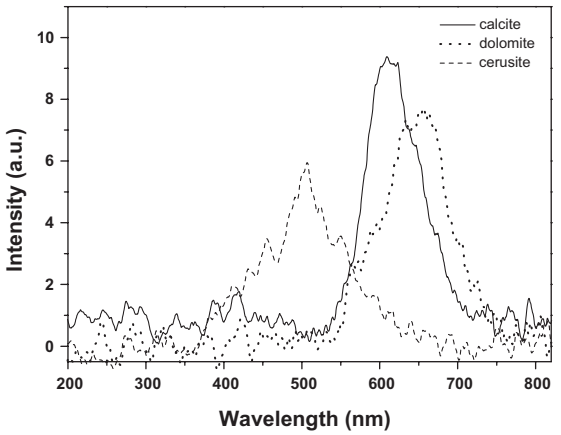

Fig. 1. Ionoluminescence spectra from carbonates collected during irradiation with 3 MeV protons.

analysis [4] and in the intense Cu yield found by PIXE, we expect that Cu is in this case involved in the light emission process.

3.2. Thermoluminescence and optical absorption

In Fig. 2(a)–(e) the TL spectra of all the carbonates before and after proton irradiation damage are shown. They are in good qualitative agreement with previous TL3D analysis [4] corresponding to X-ray irradiated samples. To the best of our knowledge there is a preliminary report on the TL of proton irradiated carbonates, but it does not offer any quantitative temperature and wavelength spectra.

Before proton irradiation, samples present a natural damage, detected at high temperature glow peaks (330–400 °C) originated by natural ionising radiation (cosmic, gamma, beta and alpha radiation) which generates high energy traps, where hole and electron states originated by irradiation have high stability.

Generally, the glow curves generated by ionising irradiation (X-ray and UV light) of carbonates consist of peaks near 130–160 °C (peak I), 250–280 °C (peak II) and 320–350 °C (peak III) [4]. Peak I is an unstable one, with a lifetime of near 3 h, whereas peaks II and III are stable, with lifetimes of the order of months [10].

In our proton irradiation experiment, using an external micro-PIXE set-up and the dose generally used for typical sample analysis, we observe the apparition of new glow peaks with respect to the ones obtained for non irradiated samples at: 300,

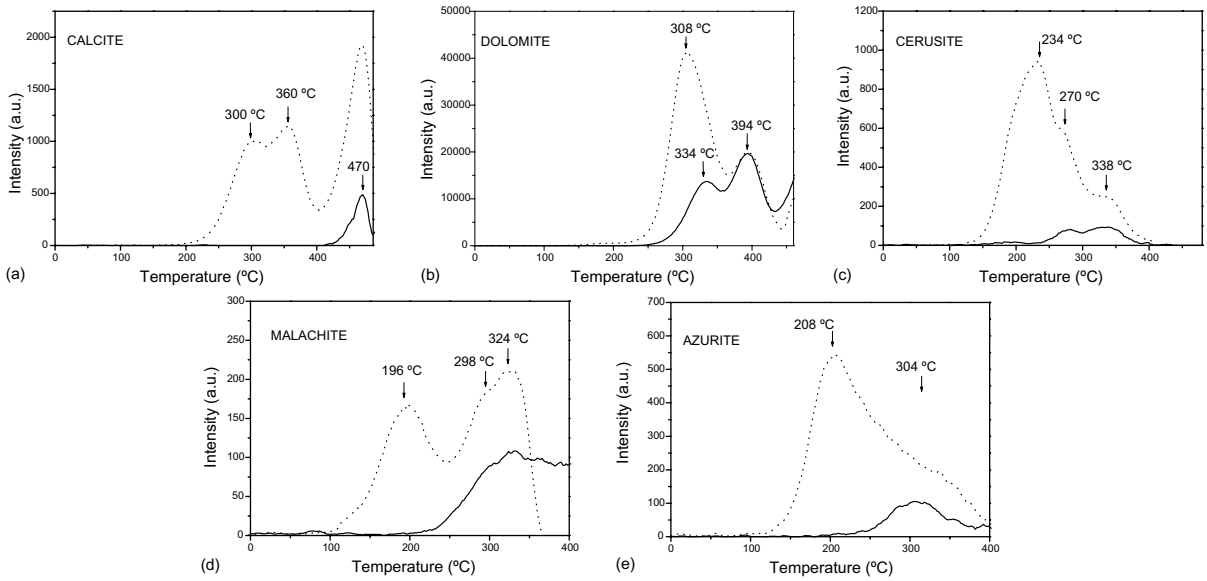

Fig. 2. Thermoluminescence glow curves from calcite (a), dolomite (b), cerusite (c) malachite (d) and azurite (e) taken before (—) and after (- - -) 3 MeV proton irradiation.

360 and 470 °C for calcite (Fig. 2(a)); 308, 334 and 394 °C for dolomite (Fig. 2(b)); 234, 270 and 338 °C for cerusite (Fig. 2(c)); 196, 298 and 324 °C for malachite (Fig. 2(d)); 208 and 304 °C for azurite (Fig. 2(e)). In this work, TL experiments were carried out 24 h after proton irradiation, in order to have a stable TL signal. Therefore peak I is not present in the glow curves shown in Fig. 2, except for malachite samples, where the elapsed time between irradiation and TL measurements was only of 1 h. Essentially the protons reproduce qualitatively the effects of X-ray irradiation, both in the structure and in the peak position of the spectra. These TL emissions can be attributed to the formation of characteristic electron traps during proton irradiation, meanwhile impurities (Mn, Pb and Cu) should be a hole recombination centre. When temperature is raised or during ionising irradiation process, electron–hole recombination takes place and luminescence can be observed.

Optical absorption measurements did not give any conclusive results. In calcite samples no clear changes were detected in optical density of the sample before and after irradiation. For cerusite, visible damage (dark spot) was created during proton irradiation in the critical conditions used to irradiate the monocrystal samples. Some changes were also observed for this carbonate in the optical density at the same region of the TL peak II, in the UV region. This coincidence between the UV absorption change with TL peaks was found in a previous work [11] in irradiated calcite and dolomite, and it is related with the apparition of colour centres, due to irradiation.

4. Conclusions

A systematic analysis of a representative set of natural carbonate minerals, traditionally used as pigments, has been done to identify the microscopic processes involved in the proton damage.

During irradiation, ionoluminescence (IL) combined with PIXE were employed to identify the impurities that act as recombination centres: Mn in calcite and dolomite, Pb in cerusite and Cu in malachite and azurite. After irradiation, it has been found that proton damage reproduce qualitatively the effects of X-ray and UV irradiation, both in the structure and in the peak position of the spectra. TL emissions can be attributed to the formation of characteristic electron traps during proton irradiation, when temperature is raised or during ionising irradiation process, electron–hole recombination takes place at the recombination centres and luminescence can be observed.

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