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Case study

Iron patinas on alabaster surfaces (Santa Maria de Poblet Monastery, Tarragona, NE Spain)

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ABSTRACT

Alabaster is a white and pure gypsum rock classically used in sculptures or for ornamental purposes, but its characteristic white colour is sometimes masked by the development of noticeable reddish stains over the surface of the rock. The main altarpiece of the Santa Maria de Poblet monastery (Tarragona, NE Spain; 16th century, Damià Forment) is the focus of this study. Red-to-ochre patinas with diameters of 2–20 cm are found on the alabaster surface of this altarpiece. The origin of such patinas are discussed, as they are the result of degradation processes of minerals present in alabaster rocks, contrary to what happens in the formation of most patinas. The patinas consist of two differentiated layers that may occur occasionally mixed. The Lower Layer contains iron compounds, which have precipitated around the gypsum crystals of the rocky support and have provided the characteristic red-to-ochre colour to the surface of the altarpiece. The formation of this layer was driven by the (bio)oxidation of the pyrite, which is disseminated over the alabaster surface. The formation of this film of iron-rich particles was conducted by a series of destructive and penetrative processes, promoting disaggregation and crystal reduction (mechanical and/or by dissolution) of the matrix minerals (gypsum, celestite, barite, calcite-dolomite...). The Upper Layer was grown by means of constructive (agglutination of particles by accretion) and destructive (destruction of the alabaster matrix and incorporation into the Lower Layer) mixed processes. Thus, the presence of small crystals (1–10 μm) of gypsum, quartz, calcite, celestite, barite, clay minerals and pyrite in this upper patina are mainly related to the residual products of the alabaster rocks. Moreover, some of the calcite, quartz and clay particles could also be considered atmospheric dust. Oxalates (weddellite and whewellite), portlandite and coal particles are not related to the formation of iron-rich patinas. Such studied patinas might date from the 19th century due to the partial destruction of the monastery after the approval of the Law of Confiscation of Religious Properties in Spain (1835) and no later than the end of the ninetieth century, when the monastery was abandoned. The entry of rainwater and presence of humidity inside the monastery would promote the pyrite oxidation processes. Currently the patinas seem to be stabilized, the pyrites are no longer in contact with water, which is needed for oxidation.

1. Introduction and research aims

The main alabaster altarpiece of Santa Maria de Poblet monastery (1527–1529, Damià Forment; Fig. 1) is a key part of Catalan Renaissance Art history [1]. Very little information exists that deals with patinas in alabaster pieces. This manuscript presents a microstructural and mineralogical characterisation of several of the red-to-ochre patinas that occur on the main surface of the alabaster altarpiece from the Santa Maria de Poblet monastery, in order to elucidate their origin, timing and future evolution, as well as to better understand how the raw material of alabaster is likely to preserve its representative white appearance over time. The term "patina" is being referred to in our work as a film or layer that covers external stone surfaces [2]. This meaning implies that the patina has a different composition to the host rock and can originate from different processes (organic, inorganic, artificial or anthropogenic, chromatic, ...) [3–5, among others].

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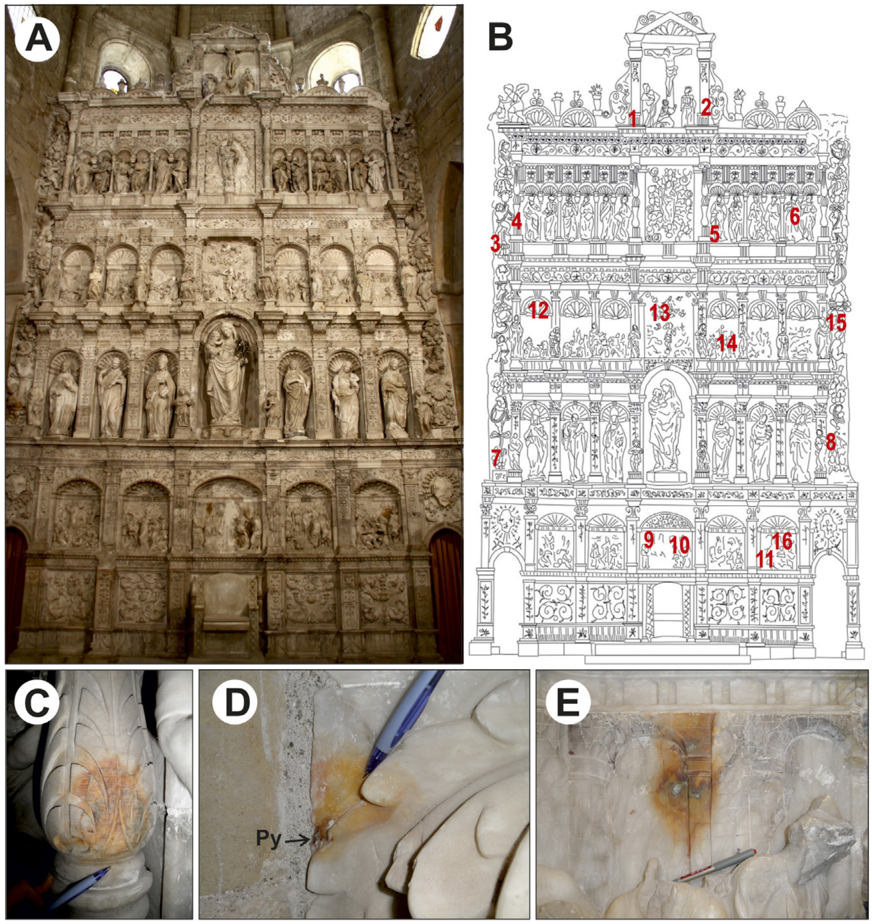

Fig. 1. A. Main altarpiece of the Santa Maria de Poblet Monastery. B. Location of the red-to-ochre patinas (red numbers in the drawing). C–E. Photographs showing the 4, 3 and 9 patinas, respectively. Py: pyrite.

2. Methods

More than 40 samples of the patinas were collected from the altarpiece. The mineralogy of selected samples was verified by means of unoriented powdered aggregates in X-ray diffraction (Siemens D-500 and Bragg-Brentano PANalytical X'Pert PRO MPD alpha1 diffractometers). Mineralogical compositions were identified with the X'Pert Highscore Plus program.

The petrographical investigation was performed on some of the objects by means of optical polarized light microscopy in covered or uncovered standard thin sections, cathodoluminescence (Technosyn Cold 8200 MkII), photoluminescence (Nikon Optiphot) and scanning electron microscopies (ESEM Quanta-200).

Two samples were examined by infrared spectroscopy (Thermo Scientific Nicolet Fourier) and a further sample was studied by Raman spectroscopy (Jobin-Yvon LabRam HR 800).

Magnetic susceptibility was measured on the altarpiece surface using a SM-20 meter (Gf Instruments). The measurements were taken across the entire surface of the altarpiece (alabaster support, patinas, joints between blocks or sculptures, holes and infillings). Units of measure are SI units.

3. Results: characterization of patinas

The altarpiece is divided into 6 levels in which, except at the base, red-to-ochre patinas with diameters of 2–20 cm have been identified. In general, patinas are irregular and randomly distributed over the altarpiece (Fig. 1). The patinas developed over an alabastrine substrate (rock composed of pure microcrystalline gypsum) [6].

The patinas are dark red-to-brown (7.5YR 3/4) in the core and lighter (ochre) outwards (from 7.5YR 7/8 to 2.5Y 8/8, after the Münsell Soil Color Chart), until they fade completely. This pigmentation is due to the presence of a significant amount of iron clearly detectable from the EDS spectra. The patinas are very superficial, only 25–300 μm thick, not penetrating far into the substrate. They show two layers, which may appear isolated, layered or mixed in the different patinas. They are, from base to top [7]:

- Lower Layer: formed by a very thin film (2–4 μm) of iron compounds, which penetrate within the alabaster substrate and surround gypsum crystals (Fig. 2). In some areas, this iron film is thicker and alters the gypsum crystals centripetally. Iron films display non-luminescence and brownish photoluminescence, and they are responsible for the noticeable red coloring. Despite the presence of iron, no relevant magnetic susceptibility signal is recorded from the patinas; measured values oscillate from 0.018 to 0.060 SI units, not very different from the background of the alabaster. Additionally, pyrite, a very common mineral in gypsum rocks, has been identified across the altarpiece in relation to the iron film. The pyrites show variable sizes from 10 μm to 3 mm (Figs. 2 and 3). The presence of pyrite is especially important because it constitutes the center part of the patina with the darkest tonality in some cases (Fig. 1D);
- Upper Layer: made of a non-oriented agglutination of small anhedral-to-euhedral crystals (1–10 μm), including gypsum, carbonate, quartz, celestite, barite, pyrite, oxalates (weddellite and