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Research Paper

Cultural heritage study: Microdestructive techniques for detection of clay minerals on the surface of historic buildings

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A B S T R A C T

Clay minerals often occur in the finishing layers covering the surface of historic and architectural artefacts. They may come from ochres intentionally applied or from atmospheric dust naturally deposited. In the first case the finishes could testify to treatments applied for the stone conservation and/or aesthetic purposes, whose study is of great interest in conservation activities.

In this paper we report on the application of microdestructive analytical techniques in order to identify the presence and the origin of clay minerals found on the surfaces of several historic buildings located in the Apulia region (Southern Italy). Optical and SEM observations, along with EDS microanalyses, and FTIR analyses were performed. The microdestructive character of these techniques made it possible to carry out the analyses on the same specimen, thus reducing the sampling. XRD analyses were also performed to confirm the presence of clay minerals. The complementary analytical findings were helpful in most cases in establishing the real origin of the clay minerals; the detection of organic materials arising from man-made treatments allowed to identify clays as pigments. However, in some cases the uncertainty remained between ochre, intentionally employed, and soil–dust deposition.

1. Introduction

Natural or artificial patinas consist in very thin finishes on the surface of historic and architectural artefacts, which are very hard to characterise due to the extremely reduced thickness and concentration of their components. Among several other constituents, clays occur in these finishing layers (Garcia-Vallès et al., 1998; Maravelaki-Kalaitzaki et al., 2001), probably coming from ochres intentionally applied or from atmospheric dust, naturally deposited. In the first case patinas could testify to ancient treatments applied for the stone conservation and/or aesthetic purposes, whose study is of great interest in conservation activities.

X-ray diffraction (XRD) is the technique usually used to identify and differentiate clay minerals, but it requires noticeable amounts of sample to give rise to detectable results. In the case of historic and archaeological artefacts studies, such as the characterisation of patinas, selective and non-destructive analyses need to be performed, due to the poor availability of the samples. Therefore, spectroscopic investigations, as well as observation by optical and electron microscopy, are preferred. The Fourier transform infrared spectroscopy (FTIR) has proved to be effective in conservation science, due to the possibility of adapting sampling methods and instrumental configurations; reliable results even on extremely low amounts of samples are provided. ESEM microscopy, coupled with EDS (Energy Dispersive Spectroscopy) microanalyses can also be applied on reduced samples and give important information on the microstructure, chemical composition and element distribution. In the case of superficial layers, a microstratigraphic study can be performed when optical microscopy facilities are deficient in terms of resolution power. Moreover, both FTIR techniques and EDS microanalysis have been successfully used as a complementary method to XRD to study clays and clay minerals (Madejová and Komadel, 2001; Madejová, 2003; Clayton and Pearce, 2007).

The present study is a part of a wider research aimed to characterise surface finishes found on the façades of historic buildings of the Apulian Region (Southern Italy). Here we report on the application of microdestructive analytical techniques in order to detect the presence and the distribution of the clay minerals within the superficial layers of the artefacts and establish if they arise from pigments intentionally applied or from soil dust. FTIR analyses, optical and electron microscope observations, along with EDS microanalyses were performed. The complementary results, obtained from analysing the same sample, were helpful in most cases in establishing the real origin of the detected minerals and, consequently, the nature of the superficial patinas. XRD analyses were also performed, in order to confirm the presence of clay minerals and to distinguish them among the silicate minerals already identified by the other applied techniques.

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2. Experimental

2.1. Sampling

The sampling of the finishes was extensive and it was usually performed in many points of each examined building. The specimens mostly included the superficial layers together with the underlying stone; only in a few cases the sampling consisted in scratching off the patina as powder from the surfaces. Here we report only the results dealing with the seven most representative samples that well describe the different situations experienced in this research.

The samples analysed come from the Cathedral in Altamura (Bari) (XIII–XIVth century), a remarkable example of the Romanesque architecture, from the churches of S. Elisabetta (XVIth century) and Santi Niccolò and Cataldo (XIIth century), in Lecce. Finally some samples were taken from the S. Giorgio church (XVIIIth century) in Melpignano (Lecce).

In Table 1 a synthetic description of the selected samples and their provenance are summarised.

2.2. Analytical techniques

Mineralogical–petrographical and stratigraphic observations were carried out by means of a Zeiss Axioplan polarizing-light optical microscope with reflected and transmitted light. Samples in either thin or polished section were analysed.

SEM-EDS observation and analyses were performed by ESEM-XL30 (FEI Company) equipped with X-Ray Dispersive Energy microanalyser (EDX), using both secondary (GSE) and backscattered (BSE) electron detectors; the low-vacuum mode (0.7 torr, 25 kV) was used on samples without metallisation using the following experimental conditions: qualitative spectra of squared areas or spots (live time 30 s) and distribution maps of the elements (matrix 256 × 220, area 700 × 560 μm, dwell 200 ms, 25 kV).

A ThermoNicolet Continuum IR microscope was used to collect the FTIR spectra in μ-ATR mode with a Si crystal; each spectrum was acquired on untreated samples in the range 4000–650 cm^{-1}, with a resolution of 4 cm^{-1} and 200 scans for each measurement. In order to minimize the contribution due to the atmospheric carbon dioxide and water vapour, a background spectrum was acquired in the air before each analysis and it was automatically subtracted (by software) from the sample spectrum. The employed instrument was not purged with dry and CO_2-free air, therefore the contribution of absorption bands of both CO_2 (appearing in the spectrum as a doublet around 2340 cm^{-1}) and water vapour (resulting in sharp and very close peaks over 3700 cm^{-1}) cannot be totally erased.

The X-ray diffraction (XRD) patterns were obtained by a Philips diffractometer (Mod. PW1729), using Cu Kα radiation (operating conditions: continuous scan, 40 kV, 20 mA, 2θ between 3° and 20°).

Table 1
Description and provenance of the samples.

Sample	Description	Provenance
1-AC	Red painted layer	Cathedral in Altamura (Bari). Main portal.
2-AC	Transparent and brown-yellow coloured patina	Cathedral in Altamura (Bari). Main portal.
3-AC	Brown–orange patina	Cathedral in Altamura (Bari). Main portal.
4-LE	Yellow–orange patina	Santa Elisabetta Church in Lecce. Rose-window.
5-LE	Yellow–reddish patina	Santa Elisabetta Church in Lecce. Façade.
6-LN	Transparent and brown-yellowish coloured patina	Santi Nicolò and Cataldo Church in Lecce. Façade.
7-MG	Brown–orange finish	San Giorgio Church in Melpignano (Lecce). Main portal.

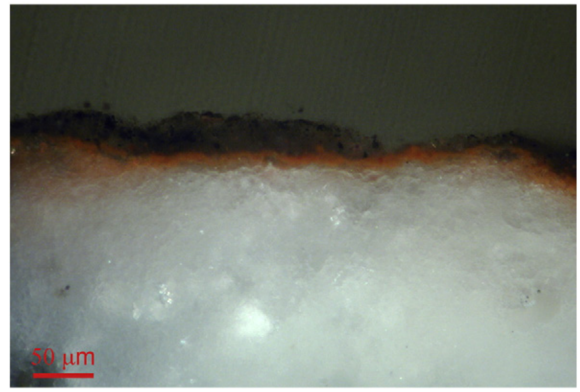

Fig. 1. Photomicrograph of the sample 1-AC, cross section, optical microscopy, reflected light.

Because of the scarcity of the samples, the analyses were carried out on the scratched powder, without any specific treatments which is used to be applied for the identification of the clay minerals.

3. Results and discussion

3.1. Coloured finishes

In the case of the sample 1-AC, a reddish layer was present on the surface. The observation of the sample in polished cross section by optical microscope allowed to identify a painted layer, containing ochre, that directly covers the stone substrate (Fig. 1).

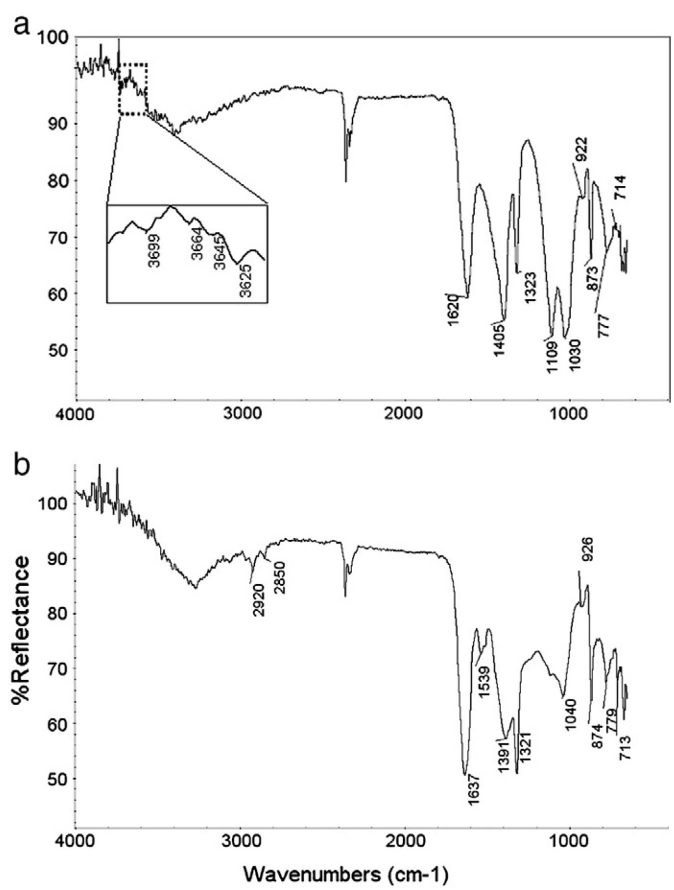

Fig. 2. FTIR analyses on the sample 1-AC, performed on: a) the layer of red colour and b) the stone substrate.