

SEM-EDX at the Service of Archaeology to Unravel Historical Technology

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Introduction

It is well known that there is a profitable cooperation between archaeology and the scientific disciplines of chemistry, geology, biology, and physics with the aim of producing better interpretations of archaeological materials. This field of science is known as archaeometry. Two main goals of archaeometry are to analyze and characterize historic objects to preserve them and to investigate the knowledge and skills required to fabricate them. This latter information is essential in the evaluation of cultural and technological aspects of past societies and to further understand the transference of technological knowledge through time periods and geographical contexts.

In the first decades of the twentieth century scientists, archaeologists, and restorers had begun to examine and analyze artworks microscopically and microchemically [1]. In the past two decades, collaboration among them has intensified, and diverse analytical methods drawn from mineralogy, petrology, and chemistry have been successfully applied to solve archaeological questions (e.g., light optical microscope, scanning electron microscopy with x-ray microanalysis, microprobe, x-ray diffraction, x-ray fluorescence, etc.). Nowadays these modern analytical techniques are considered to be standard and irreplaceable for the characterization of ancient materials. This is the case for microscopic techniques that provide essential information on artwork microtexture, microstructure, and composition, thus yielding key information regarding manufacturing methods and best practices for object conservation.

Art and archaeological objects comprise a wide variety of such composite materials as stone, ceramics, bricks, paintings, metals, coverings, etc., made up of natural or artificial (inorganic or organic origin) components. The analytical investigation of these artworks can be a challenging task, particularly when their components are present as micro- to nano-sized components or at trace amounts. Therefore, the application of cutting-edge analytical techniques or novel analytical routines offers new possibilities to attain a fully comprehensive materials characterization that can be applied to the archaeological/historical problem to be resolved [2, 3].

The aim of this article is to show how the scanning electron microscope combined with energy-dispersive x-ray spectrometry (SEM-EDX) can be used to obtain important information from archaeological samples, namely paintings and wall coating from the fourteenth-century Nasrid period (during Muslim rule from 1238 to 1492) at Granada, Spain. Mineral

maps produced in the SEM-EDX provided key information concerning the distribution of minor mineral phases, grain size and grain shapes, and microtextural and structural characteristics that may be overlooked when performing single-point analyses or elemental maps in artwork materials. Though mineral maps have been employed somewhat in geology [4], they have not yet been applied in heritage science. Their use opens new possibilities for better artwork characterization.

Experimental

Light optical microscopy (LOM) in transmitted and reflected light (Olympus BX60; photography with Olympus DP10) was used to examine the petrographical characteristics, materials composition, and state of conservation of the studied materials. Later, a detailed analysis of the microtexture and chemical composition was performed with a LEO 1430VP scanning electron microscope (VP-SEM), coupled with an Oxford Instruments INCA 350 EDX microanalysis system version 17, which allows identification of elements with low atomic numbers, including carbon. Images were obtained in backscattered electron (BSE) and secondary electron (SE) modes. For the analysis of the materials, polished thin sections (without carbon coating) were prepared to allow the study of sample cross-sections. Single point elemental analyses and x-ray maps were acquired with 5×10^{-3} mbar of N_2 in the specimen

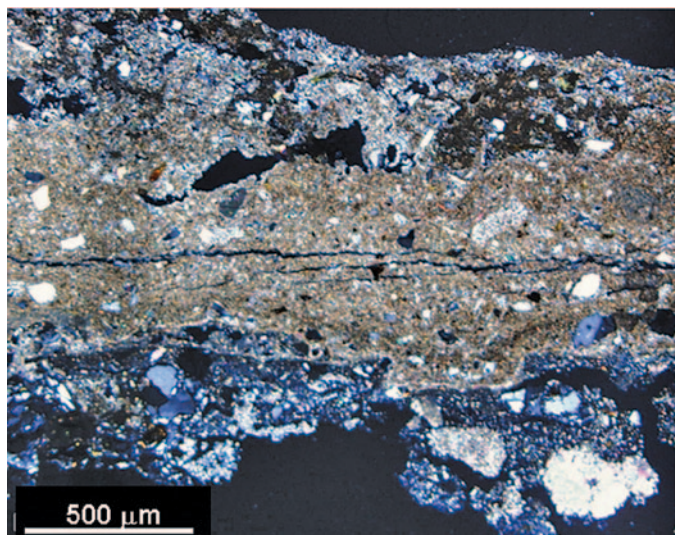


Figure 1: Light optical microscopy photograph showing the cross-section of the Islamic wall coating (transmitted light under crossed polars, TL-CP).

chamber to avoid charging. The SEM-EDX working conditions were 20 keV beam energy, 500 pA beam current, and 10 eV/ch spectrum energy acquisition for pinpoint analyses. For map acquisition, a beam current of 1 nA beam was used. High-resolution x-ray maps (1024 X 768 pixels) were obtained in selected areas with 500 frames acquired over 16h.

The *Phasemap* tool in the INCA 350 system identifies mineral phases using ternary element plots of specific pixel information from montaged x-ray maps. The procedure for mineral map acquisition involves the use of so-called “ternary phase diagrams.” The software generates mineral maps of relative concentrations for up to three elements specified by the user. The element information embedded in each image pixel is rearranged in such a way that regions of similar (ternary) composition can be determined in the phase diagram. Superposition of images obtained from different “ternary phase diagrams,” represented as a false color map, then yields a “phase map.” To give a realistic reconstruction of mineral distribution in the cross-sectioned sample, the obtained mineral map can be “mixed” into the BSE image. Quantitative analysis was done with the *Point & ID* tool in the software. For the wall coating characterization, improved quantitative results were obtained using *ad hoc* real standards instead of the virtual pack standards supplied with the INCA software.

Case study 1: characterization of a Medieval Islamic wall coating.

Recent archaeological excavations alongside the Alberzana wall, built in the Albayzín quarter of Granada (a UNESCO World Cultural Heritage site), Spain, by fourteenth century Nasrids, discovered a brick oven among other ruins. *In situ* examinations revealed evidence of melting processes in the bricks,

indicating furnace temperatures well above those required to fire Nasrid bricks and pottery (~ 800 °C). Adjacent to the oven, a well-defined stratigraphic sequence comprising layers of black ash and remains of bones suggest that the oven was used to fabricate a special coating for the wall that included burnt animal bones. To test this hypothesis, innovative analytical protocols were employed for characterizing the covering and bricks using complementary non- and micro-destructive spectroscopic and diffraction analytical techniques [3].

This case study is of significant interest for archaeologists since the occurrence of powdered burnt bones have been identified in Greco-Latin, Ibero-Celtic, and Medieval Christian monuments, either added as a hardening material or with aesthetical intention to confer a warm ochre tone [5], but never, to the authors' knowledge, in Medieval Islamic constructions. More importantly, unlike the present case, the literature reports neither archeological evidence of bones used as raw materials nor ovens to burn them.

Visual inspection revealed an orange-brown coating of about 1-mm thickness. The LOM study (Figure 1) showed that calcite (CaCO_3) constituted the binder and part of the aggregates and where microfossils were also present. Other identified aggregates were quartz (SiO_2) and micaschists (low-grade metamorphic rock). These observations suggest the use of geological materials from the immediate vicinity. Then pinpoint analysis using SEM-EDX revealed ubiquitous Ca in the coating (as binder and aggregate), attributed to calcite. Silicon was detected in the most abundant, largest, and irregularly shaped particles, with a broad grain size distribution (~10–100 μm), suggesting the presence of quartz as an aggregate. Fewer smaller particles (<10–50 μm) containing Mg also were identified and interpreted as dolomite, $\text{CaMg}(\text{CO}_3)_2$. Scarce acicular crystals composed of Al, Si, Mg, and K were interpreted as illite (a mica-type clay mineral). In the SEM images, a few angular grains of variable crystal size below 15 μm in diameter were seen. The pinpoint EDX analyses identified Fe and Ti in these grains, attributed to hematite (Fe_2O_3) and rutile (Ti_2O), respectively. Phosphorus (P) was identified in the finest particles (<10 μm) dispersed in the coating. These particles, not easily observed with LOM because of their small crystal size, were clearly identified in the compiled mineral map produced from SEM-EDX elemental maps.

Because one of the main goals of this work was the identification and visualization of hydroxyapatite ($\text{Ca}_{10}[\text{PO}_4]_6[\text{OH}]_2$), the main bone component, EDX spectral intensity ratios measuring relative concentrations of Ca, P, and O were extracted from the raw data for each pixel and plotted in a ternary composition diagram. Similarly, Ca-K-Si and Mg-Ca-Si ternary phase diagrams were plotted to visualize the distribution and morphology of quartz, calcite, dolomite, and illite. Figure 2 shows the ternary phase diagrams and the resulting mineral map. The false-color map shows that calcite was the most abundant mineral (95.44%) and was evenly distributed in the

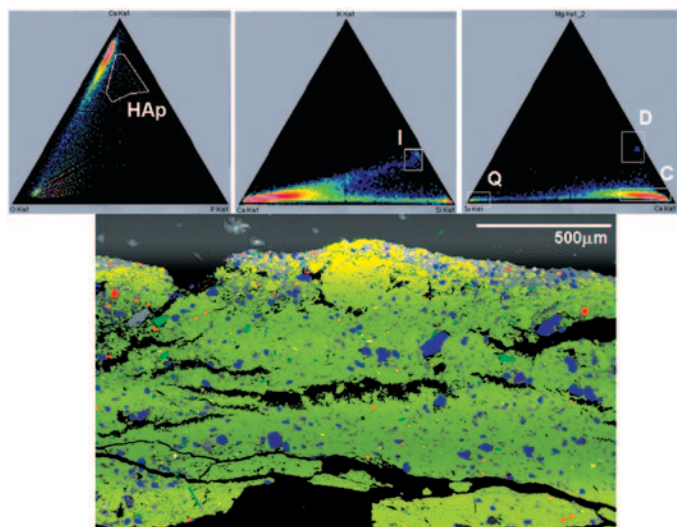


Figure 2: Ca-P-O, Ca-K-Si, and Mg-Ca-Si ternary phase diagrams (top). White boxes enclose the spots that correspond to the different mineral phases, namely, HAp = hydroxyapatite-like mineral; I = illite; Q = quartz; D = dolomite; C = calcite. False-color mineral map produced from SEM-EDX elemental mappings in the cross-section of the coating (bottom). Pistachio represents C, red represents HAp, blue represents Q, purple represents D, and green represents I.

coating. Hydroxyapatite was very scarce (0.33%) and randomly distributed as discrete, smoothed grains of sizes smaller than 40 μm . Other finely divided grains visualized in the map were uneven particles of angular quartz (3.48%), angular dolomite (0.48%), and needle-shaped illite (0.46%). Percentages were balanced considering the contribution of the image black background. This imaging method efficiently identifies components, their distribution, morphology, and abundance; however, the exact mineral composition cannot be established from the maps alone.

Case study 2: characterization of Nasrid pigments in the Alhambra monument

The Alhambra represents the grandest and finest example of Islamic art and architecture from the Middle Ages still standing in the Western world. However, scientific publications on pigment composition and painting techniques used by the Nasrids to polychrome their artworks in the Alhambra are sparse [3, 6]. To fill in gaps in the knowledge of Nasrid art (traditionally approached by stylistic studies), to clarify historical and painting uncertainties in the Alhambra, and for conservation purposes, it is essential to obtain an in-depth characterization of the painted artwork. Previously published work [6], combining LOM and SEM-EDX-based mineral maps, analyzed painting materials, manufacture, deterioration processes, and distinctive morphotextural characteristics.

We present here the results of a paint stratigraphy [6] where LOM shows (Figures 3a and 3b) a well-preserved white layer ($\sim 75 \mu\text{m}$ thick) identified by SEM-EDX as white Pb-based pigment. The lead speciation (e.g., cerussite, hydrocerussite,

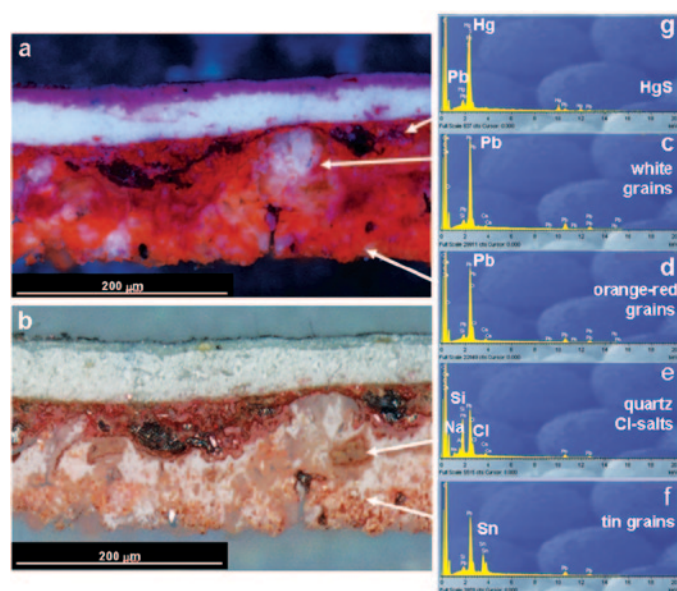


Figure 3: EPhotomicrographs showing the Nasrid paint stratigraphy: (a) under TL-CP; (b) under reflected light uncrossed polars. From the inside out, the layer sequence is: red lead base layer, vivid red layer made of cinnabar, and a white lead layer at the surface. SEM-EDX spectra of (c) white grains, (d) orange-red grains, (e) quartz particles and chloride-based salts, (f) tin grains, and (g) red grains.

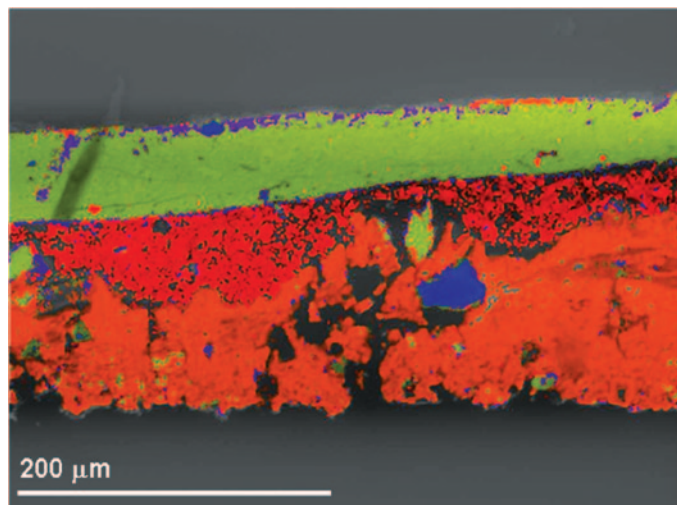


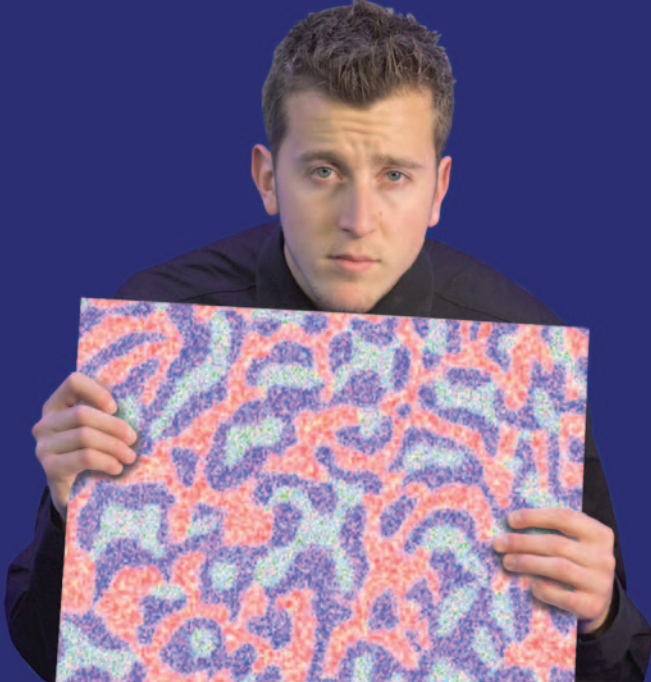
Figure 4: EA false-color mineral map of the Nasrid paint sample based. Orange represents red lead, blue represents quartz, green represents a white Pb-based pigment at the outside surface, and bright red represents cinnabar.

etc.) could not be established due to limitations of the SEM-EDX technique. Below this there is a vivid red layer containing angular particles ($\sim 5\text{--}30 \mu\text{m}$) identified with SEM-EDX as mercury sulfide (cinnabar). Finally, on the bottom, the ground layer was found to be a well-mixed mass of irregularly shaped orange-red and white grains, which suggests that it was made of improperly manufactured red lead (Pb_3O_4). This pigment is produced by heating white lead (cerussite, PbCO_3) in the presence of air. When red lead is produced under insufficient heat, red-orange oxide forms (orange lead), and white grains can remain embedded in the matrix (as seen in Figure 3a).

SEM-EDX pinpoint analyses confirmed the presence of Pb in both the orange-red and the white grains. Also, Si was detected in some of the largest particles (Figure 3e), which suggests the presence of quartz added as extender to give more body to the layer. The compiled mineral distribution map (Figure 4) allows better examination of these grain distributions. The false colors of this figure were selected in such a way as to reproduce the original paint stratigraphy most realistically. Thus, the ground layer made of red lead is shown in an orange color, dispersed coarse blue grains attest to the presence of quartz, and smaller green grains correspond to white Pb-based pigment. Next appears the cinnabar-based layer in vivid red with scarce blue grains of quartz. At the top there is the white Pb-based paint layer in green color.

During the SEM study of the matrix, an in-depth examination of the x-ray emission spectra of Pb in the orange-red particles and in the white particles revealed interesting spectral differences between them. It was systematically observed that the Pb M γ spectral line was more intense in the orange-red grains than in the white grains when intensities were normalized to Pb M α –M β peaks (Figure 5). The Pb M γ line corresponds to a transition from a valence shell, whereas the Pb M α and M β spectral lines correspond to electronic

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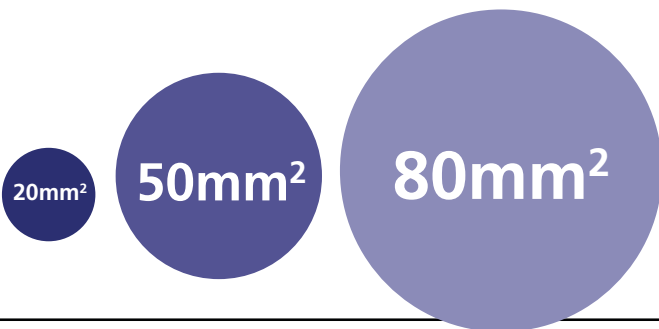
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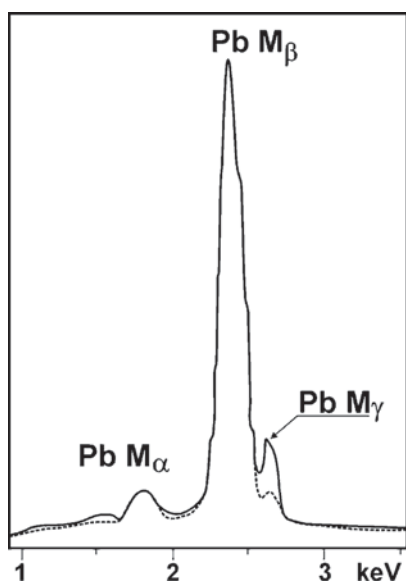


Figure 5: X-ray emission spectra of Pb for the orange-red and white pigments from the ground layer of the paint sample, showing the Pb M_{α} , M_{β} and M_{γ} spectral lines normalized to the intensity of the Pb M_{α} - M_{β} peak. The Pb M_{γ} spectral line is more intense in the red pigment (solid line) than in the white pigment.

transitions between atomic core-levels. Electronic transitions from valence levels depend upon the Pb chemical environment and, therefore, on the nature of the chemical bonds between Pb and the surrounding anions. Thus, we propose that the Pb M_{γ} spectral line could be used as a diagnostic method to discriminate between red (oxides) or white (carbonates) in Pb-based pigments.

This study indicates that the rich information about materials enshrined in x-ray emission spectra may be studied in a straightforward manner by phase map analysis. In this sense, phase map analysis constitutes a novel methodology, which further highlights the benefits of the applying of SEM-EDX technique to the study of artworks.

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References

- [1] G Dijkstra, and J Mosk, *Trends Anal Chem* 1 (1981) 40–44.
- [2] M Cotte, J Susini, N Metrich, A Moscato, C Gratzu, A Bertagnini, and M Pagano, *Anal Chem* 78 (2006) 7484–7492.
- [3] C Cardell, I Guerra, J Romero-Pastor, G Cultrone, and A Rodriguez-Navarro, *Anal Chem* 81 (2009) 604–611.
- [4] R G Smeink, Van GC Leerdam, and JWG Mahy, *Miner Eng* 18 (2005) 247–255.
- [5] J Martin-Gil, FJ Martin-Gil, MC Ramos-Sanchez, and P Martin-Ramos, *Environ. Sci Pollut Res* 12 (2005) 285–289.
- [6] C Cardell, L Rodriguez-Simón, I Guerra, and A Sánchez-Navas, *Archaeometry*, doi: 10.1111/j.1475-4754.2008.00438.x.0.

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