

FOCUS: MICROSCOPY AND IMAGING

Comparing the Detection of Iron-Based Pottery Pigment on a Carbon-Coated Sherd by SEM-EDS and by Micro-XRF-SEM

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The same sherd was analyzed using a scanning electron microscope with energy dispersive spectroscopy (SEM-EDS†) and a micro X-ray fluorescence tube attached to a scanning electron microscope (Micro-XRF-SEM) to compare the effectiveness of elemental detection of iron-based pigment. To enhance SEM-EDS mapping, the sherd was carbon coated. The carbon coating was not required to produce Micro-XRF-SEM maps but was applied to maintain an unbiased comparison between the systems. The Micro-XRF-SEM analysis was capable of lower limits of detection than that of the SEM-EDS system, and therefore the Micro-XRF-SEM system could produce elemental maps of elements not easily detected by SEM-EDS mapping systems. Because SEM-EDS and Micro-XRF-SEM have been used for imaging and chemical analysis of biological samples, this comparison of the detection systems should be useful to biologists, especially those involved in bone or tooth (hard tissue) analysis.

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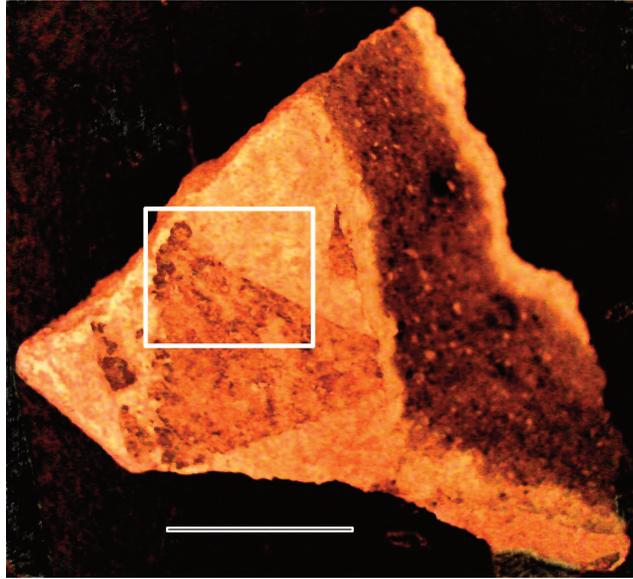
†Abbreviations: EDS, energy dispersive spectroscopy; SEM, scanning electron microscope; SEM-EDS, scanning electron microscope with energy dispersive spectroscopy; Micro-XRF-SEM, micro X-ray fluorescence tube attached to a scanning electron microscope; Si(Li), lithium-drifted silicon; XRF, X-ray fluorescence; LA-ICP-MS, laser ablation-inductively coupled plasma-mass spectrometry; MDL, Minimum Detection Limits.

Keywords: scanning electron microscopy, pottery pigment, archeology

Author contributions: MWP completed the SEM-EDS map and light microscope image, DKW supplied the sherd sample and archeological expertise, EAE provided expertise in carbon evaporation, and BBP provided manuscript continuity assistance.

Figure 1. Light microscope image of iron-based painted sherd before carbon coating.

Portion of sherd shown in Figures 2 and 3 is within white rectangle. Scale bar = 5 mm. From: Pendleton MW, Washburn DK, Ellis EA, Pendleton BB. Distinguishing Between Mineral Paint and Carbon Paint on Ancestral Puebloan Pottery. *Microscopy Today*. 2012;20:32-6. Reprinted with the permission of Cambridge University Press.



INTRODUCTION

The typological classification of ancestral Puebloan black-on-white painted pottery of the American Southwest is often determined by the variety of pigment used to make the painted patterns. The pigments are usually defined as two principal types: carbon-based (organic derived), mineral-based (commonly containing iron), or a mixture of both types [1]. The usual method of determining the type of pigment on a piece of Southwestern pottery has been visual characterization based on two traditional definitions. Carbon-based pigments seem to penetrate into the pottery matrix and have poorly defined edges [2], while mineral-based pigments have a flaky surface texture [3]. Pottery pieces with pigment that cannot easily be determined visually to be either paint type include examples with both types (mixed) of pigment or are badly weathered. Stewart and Adams [1] validated the visual pigment classifications by comparing them to those determined by SEM-EDS. The accuracy of visual classification was 84.2 percent for fifteen Mesa Verde White Ware sherds from Wallace Ruin, Colorado. However, many other researchers of Southwest American pottery such as Shepard [2], Nelson [4], and Roney [5] noted that the classification of paint pigment by visual means can be inadequate.

In this study, we compared EDS-SEM and Micro-XRF-SEM elemental maps of an ancestral Puebloan pottery sherd. The primary difference between EDS-SEM and Micro-XRF-SEM is the excitation method. EDS-SEM uses electrons to excite the sample, while Micro-XRF-SEM uses X-rays. In both methods, characteristic X-rays are generated by the elements in the sample which are then collected and analyzed by the EDS detector. This comparison of the imaging and element mapping for EDS-SEM and Micro-XRF-SEM systems has relevance for samples other than pottery, such as biological and medical (hard tissue) samples [6].

MATERIALS AND METHODS

An ancestral Puebloan black-on-white pottery sherd from the American Southwest was used for this study because the painted surface closely matched the visual characteristics designated by Shepard [2] for mineral-based paints that contain iron. The term “black-on-white” refers to the application of a black pigment to a lighter colored pottery matrix. A Proscope digital camera (Ted Pella, Redding, California) was used to make the light microscopy image (Figure 1) of the sherd before coating it with carbon to demonstrate the location of the dark-colored iron-based paint pigment in relation to the

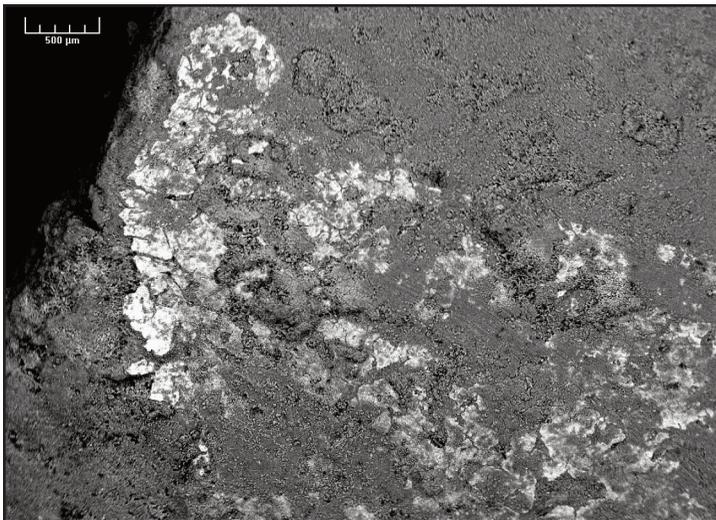
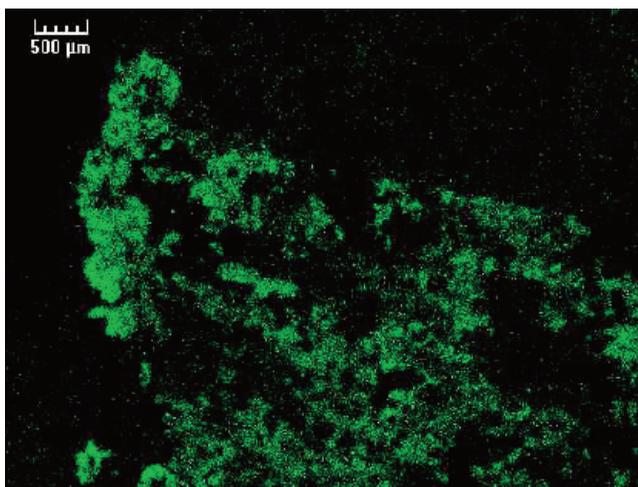


Figure 2. Backscatter SEM image of the carbon-coated sherd. Location of paint pigment containing elements (such as iron) possessing a greater average atomic number than the surrounding matrix shown by a brighter grey scale (compositional contrast). Scale bar = 0.5 mm.

Figure 3. Iron SEM-EDS map of carbon-coated sherd. Location of paint pigment containing iron is shown by green dot pattern. Scale bar = 0.5 mm.

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relative position of the backscatter and iron SEM-EDS and Micro-XRF-SEM maps. A JEOL JSM-6400 high-vacuum SEM with a tungsten filament operating at 20 kV accelerating voltage equipped with Princeton Gamma Tech (PGT) Spirit imaging software was used to produce a backscatter (Figure 2) image of the sherd. A PGT SEM-EDS detector with a lithium-drifted silicon (Si(Li)) crystal produced (at 20 kV for 30 minutes for optimal results) the SEM-EDS map showing the location of iron (Figure 3) on the carbon coated sherd. The rectangle in Figure 1 indicates the area examined for the backscatter image and SEM-EDS map. A Cressington 308R coater was used to apply a 40 to 50 nm thick evaporative carbon coating to control charging (loss of detail caused by excess surface electrons) on the sherd

during SEM-EDS mapping. This was the minimum coating thickness to control charging of the sample.

Using the same sherd sample used to generate the images and SEM-EDS map, several Micro-XRF-SEM maps (Figures 4-6) of iron and several elements, including sulfur, calcium, and potassium, were generated (using 50 keV) by using an X-ray source aimed at the sherd (IXRF Systems 10 micron X-beam Micro-XRF) and mounted to a Hitachi S-3400N SEM. X-rays were collected using an IXRF Systems (30 mm) EDS detector that produced the elemental maps. The IXRF Systems EDS detector was able to obtain elemental maps of the entire sherd during a period of 19 hours (using a high-resolution setting and a long point dwell) to produce extremely good quality el-

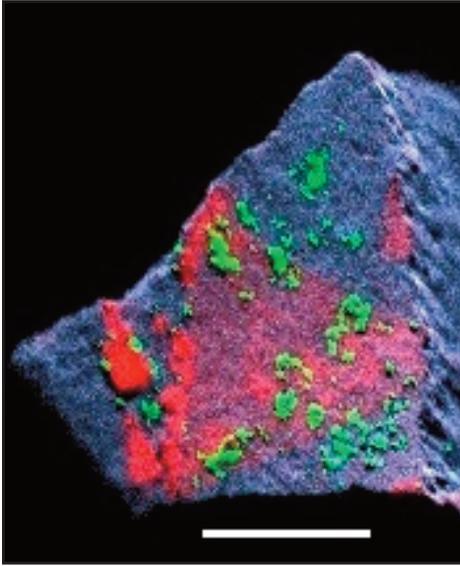


Figure 4. Micro-XRF-EDS map of carbon-coated sherd. Location of paint pigment containing iron is shown by red dot pattern, location of paint pigment containing sulfur is shown by green dot pattern. Location of sherd matrix is shown by blue shading. Scale bar = 5 mm.

emental maps. Similar maps could be produced with some changes to collection parameters that substantially reduce acquisition time. While laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) can identify elements in pottery pigments [7], the system is not as commonly available as SEM-EDS or Micro-XRF-SEM and the laser removes (ablates) small portions of the sample, which may not be permissible for culturally important samples. And while microhysteresis [8] can identify elements in pigments that respond to a magnetic field, this system is also not as common as the SEM-EDS or Micro-XRF-SEM systems.

RESULTS

A comparison of the dark iron-based pigmented areas within the rectangle in Figure 1 correlates well with the lighter grey areas (containing iron, which has a larger average atomic number than the pottery matrix) in the backscatter SEM image (Figure 2). The pigmented areas within the rectan-

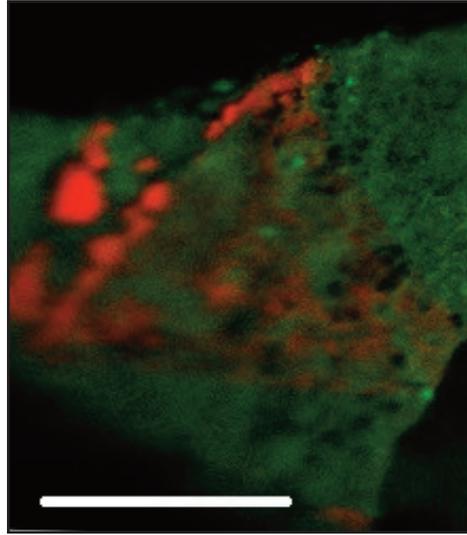


Figure 5. Micro-XRF-EDS map of carbon-coated sherd. Location of paint pigment containing iron is shown by red dot pattern, and location of paint pigment containing potassium is shown by green dot pattern. Scale bar = 5 mm.

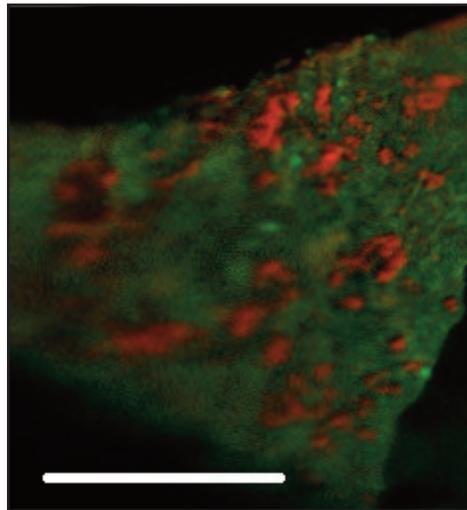


Figure 6. Micro-XRF-EDS map of carbon-coated sherd. Location of paint pigment containing calcium is shown by red dot pattern, and location of paint pigment containing potassium is shown by green dot pattern. Scale bar = 5 mm.

gle in Figure 1 also correlate well with the bright green pattern in the SEM-EDS iron elemental map (Figure 3). The iron-pigmented area shown on the surface of the sherd in Figure 1 also correlates well with the pattern of iron on the Micro-XRF-SEM

maps (Figures 4-5). The other Micro-XRF-SEM elemental maps of other elements (calcium, sulfur, and potassium) (Figures 4-6) demonstrate the locations of the elements that are not correlated with the pigment pattern shown in Figure 1 but are present in the matrix of the pottery sherd.

CONCLUSIONS AND OUTLOOK

Both SEM-EDS and Micro-XRF-SEM analysis can be used to produce iron EDS maps of the patterns of iron-based pigments on American Southwest prehistoric pottery. Although SEM-EDS could produce a map of only iron (Figure 3) in the painted area of the sherd, Micro-XRF-SEM was able to detect not only iron, but also sulfur, calcium, and potassium (Figures 4-6). While elements other than iron were on the maps in areas not correlated to the painted portions of the sherd, they represent concentrations of elements within the pottery matrix. This superior level of detection of elements other than iron by Micro-XRF-SEM is because of the lower background of XRF compared to that of electrons generated by the SEM beam (in SEM-EDS). The lower background of XRF allows trace elements to be detected and mapped. Elements with atomic numbers larger than silicon have greater excitation efficiency with more than 2 kV accelerating voltage with a true X-ray beam (XRF) compared to an electron beam. For accelerating voltages greater than 2.0 kV, the decelerating electrons entering the sample become less efficient at exciting the electrons in orbitals of the sample, so this produces the background that prevents detection of trace elements. The Minimum Detection Limits (MDL) of an electron beam are about 1000 parts per million (ppm) or 0.1 weight percent while XRF has a MDL less than 100 ppm [9]. Because of this low MDL, Micro-XRF-SEM is more effective in identifying the location of iron-based paint pigment as well as concentration of other elements in the pottery matrix of ancestral Pueblo pottery from the Southwest United States. This effectiveness is demonstrated by the more even and resolved maps produced

by Micro-XRF-SEM (Figures 4-6) than by SEM-EDS (Figure 3).

The Micro-XRF-EDS maps (Figures 4-5) show the iron pigment at greater depth while the SEM-EDS map (Figure 3) shows only the location of iron pigment flakes on the surface of the sherd. The greater depth of the X-ray penetration depends on the sample matrix, but for samples containing elements with low atomic numbers, an XRF analysis can be made as deep as 2 mm within a sample [10].

In this study of an iron-based painted sherd, Micro-XRF-EDS maps of potassium in Figures 5 and 6 locate small concentrations of potassium in the pottery matrix. Potassium has been determined to be an effective marker element using SEM-EDS to identify the location of carbon-based (organic) pottery pigment [11]. Using an XRF system (equipped with a synchrotron X-ray source rather than the tube X-ray source used in our study), potassium, copper, and manganese elemental maps were generated that located carbon-based (organic) pigment on a Southwestern prehistoric sherd [12]. While these researchers [12] presumed the potassium was from plant sources, they did not mention that potassium was determined to be present in the highest concentration [13] of all elements in an analysis of modern Rocky Mountain beeweed (the likely plant used to produce organic pigment), which was the significant factor that confirmed the role of potassium as a marker for carbon-based pigment [11].

While carbon coating was required to reduce charging during production of the SEM-EDS map, the coating was not needed for creating the Micro-XRF-SEM map. Sherds with cultural importance and/or currently in a museum display could be analyzed by Micro-XRF-SEM without obscuring the paint with carbon so the sherd would be visually unchanged for subsequent viewing. For biological and medical samples, the detection of trace elements using Micro-XRF-SEM systems [6] can offer significant advantages over SEM-EDS systems. For example, Roschger et al. [6] were able to detect a concentration of physiolog-

ical endogenous strontium in bone at a level below the sensitivity range of SEM-EDS by using a synchrotron radiation-induced Micro-XRF-SEM in their study of bone material quality of women following strontium ranelate treatment.

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