Distinguishing between Mineral Paint and Carbon Paint on Ancestral Puebloan Pottery

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Introduction

Archaeologists have found that the elements present in the pigments used on Ancestral Puebloan black-on-white painted pottery are an important descriptive attribute. They typically describe the pigments used to produce these painted designs as either carbon-based (containing primarily organic compounds) or mineral-based (containing primarily iron compounds), although in some cases these pigments are combined or "mixed" [1].

Determination of the type of pigment has traditionally been done by visual inspection. Iron-based paints appear to "sit" on the surface, and the designs have sharp edges, whereas carbon-based paints appear to "soak" into the surface and appear to have fuzzy edges [2]. These identifications can be validated using scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) [1]. Although Stewart and Adams [1] previously used SEM-EDS to characterize mineral-based paints on pottery by the detection of iron, this paper uses SEM-EDS to detect potassium as a marker element for carbon-based paints using a few novel changes in methodology.

Materials and Methods

A JEOL JSM-6400 SEM with a tungsten filament and a PGT (Bruker) Si(Li) EDS system employing Spirit software were used to compare the SEM-EDS spectra and elemental maps of both mineral- and carbon-based paint pigments. Because mineral-based paints do not sink into the surface of the pottery but remain on the surface [3], 15 kV accelerating voltage was used to penetrate only the outermost pigmented layer of the sherd to produce spectra of painted and unpainted areas. However, because carbon-based paints are thin and sink into the clay body of the pottery [3], 35 kV accelerating voltage is required for deep beam interaction to produce SEM-EDS spectra of potassium dispersed within the fabric of the sherd.

Results

Detection of mineral-based paint. A prehistoric southwestern U.S. black-on-white painted pottery sherd was selected for this study because its pigment characteristics matched the attributes described by Shepard [2] for iron-based paint. Carbon coating was applied to this sherd to reduce charging. A light microscope image of this mineral-based painted sherd is shown in Figure 1 prior to carbon coating in order to display the location of the dark-colored mineral-based pigment areas. The rectangle in Figure 1 indicates the area examined by SEM-EDS mapping. The SEM-EDS map (Figure 2) shows more iron in the brighter yellow area that correlates well with the pigmented areas of the sherd within the rectangle in Figure 1. The SEM-EDS spectrum from within the painted area (Figure 3a) has a higher peak for iron than does the SEM-EDS spectrum taken within the unpainted area (Figure 3b).

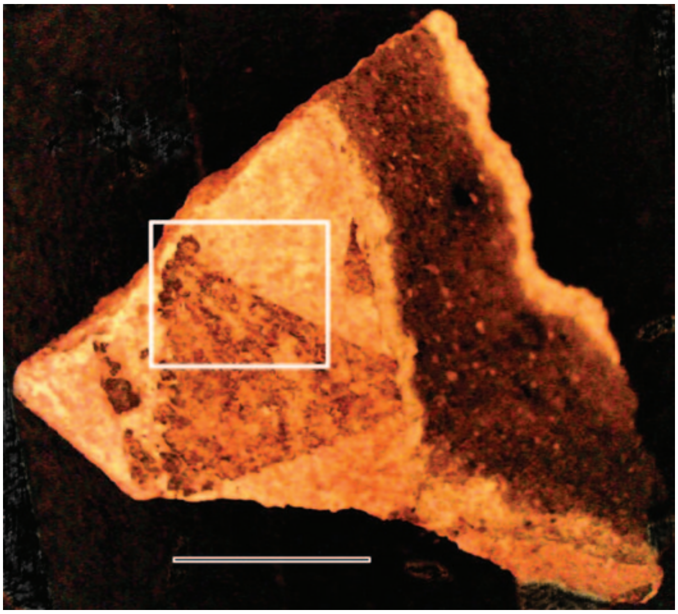

Figure 1: Mineral-based painted sherd prior to carbon coating. Rectangle defines area of Fe X-ray map in Figure 2. Scale bar = 5 mm.

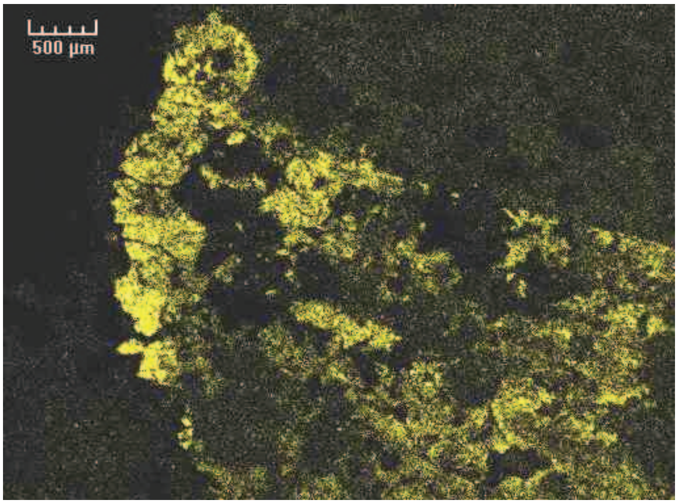

Figure 2: Iron X-ray map showing areas of higher Fe content (bright yellow area). Scale bar = 500 µm.

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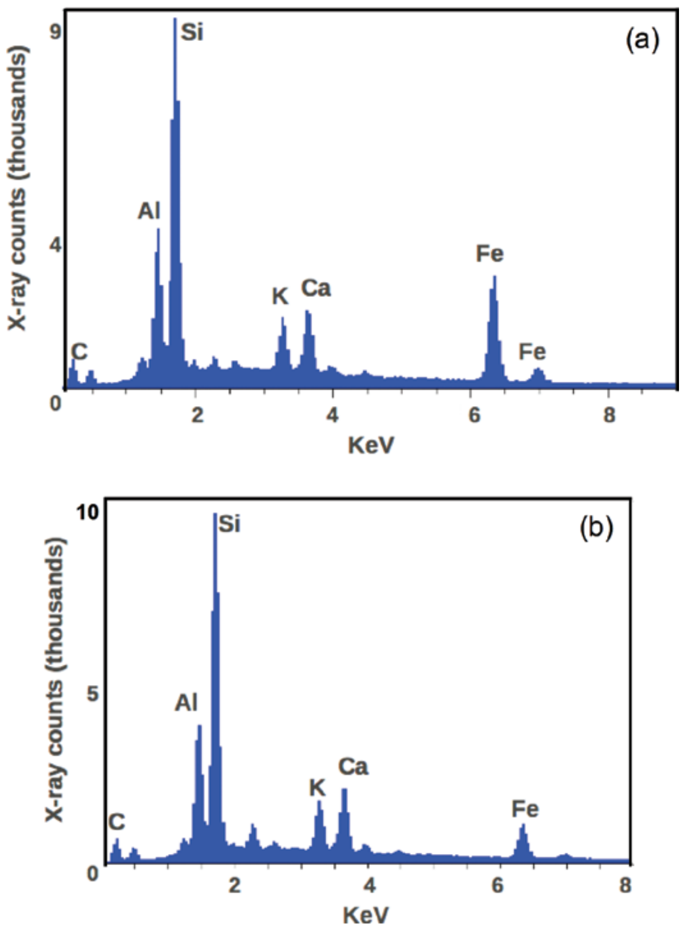

Figure 3: (a) EDS X-ray spectrum of pigmented area of mineral-based paint. (b) EDS X-ray spectrum of un-pigmented area of mineral-based paint (15 kV).

Detection of carbon-based paint. Blair and Blair [4] note that "carbon black" is not descriptive of the chemical makeup of carbon-based pottery paint because the carbon that has not burned off contributes in only a minor way to the black color. Because carbon is only present in low concentrations in carbon-based paint, it is difficult to directly detect as a distinct X-ray peak in painted and unpainted surfaces using SEM-EDS detection systems.

Stewart and Adams [1] used SEM-EDS to demonstrate that a higher average ratio of carbon-to-silicon can be found for the carbon-based painted area compared to the unpainted area of a sherd. They obtained similar results with a modern replicate sherd painted with carbon paint prepared with a Rocky Mountain beeweed (*Cleome serrulata* Pursh) plant. In contrast, our study demonstrates that SEM-EDS can produce spectra and maps that differentiate carbon-based pigment using potassium as a marker element.

In the Ancestral Pueblo area of the northern Southwest, carbon-based pigments are commonly thought to have been derived in prehistoric times by boiling the crushed leaves, stems, and roots from the Rocky Mountain beeweed plant so that, as the material is boiled, the juice becomes the paint, which is then applied to the pottery surface [5]. These carbon-based paints therefore contain significant levels of the elements extracted from the plant cells. Because potassium is the most abundant cation in cells of the higher plants [6], potassium is still abundantly present following the paint extraction by boiling. Previous analysis by inductively coupled plasma-atomic emission spectroscopy of three samples of boiled modern Rocky Mountain beeweed extract showed that potassium has the highest concentration (ppm of mg/kg of undigested sample) of all elements detected [7].

In previous studies, the use of this carbon-based pigment could only be suggested by the absence of any mineral pigments (iron) in the darkly painted areas of pottery [8]. In their study, Stuart and Adams [1] assumed that the absence of iron in SEM-EDS spectra of pottery pigment indicated by default that the paint is carbon-based.

Further, while Stuart and Adams [1] used an evaporative coating of carbon on the sherds prior to acquisition of EDS spectra, they noted that for carbon-based pigments the carbon X-ray signal from the evaporative carbon coating could not be distinguished from that of the paint. For sherds painted with carbon-based pigments without an evaporative carbon coating, van der Weerd et al. [8] found that the elemental SEM-EDS carbon signal was masked due to surface carbon contamination, especially in excavated sherds.

To avoid this problem, in our study no carbon coating was applied to the carbon-based painted sherd. Thus, if carbon were detected by SEM-EDS, it would not be due to the coating. In this study, the reduction in charging of the sherd was accomplished by the addition of aluminum foil and metal tape to its periphery (Figure 4). This approach also allowed the uncoated archeological sherd to retain its original surface condition following analysis so it could be returned to the museum display.

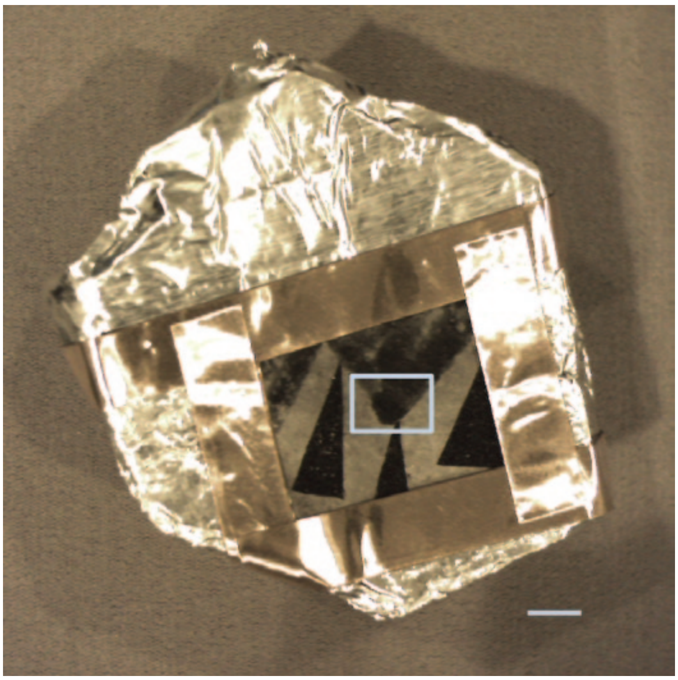

Figure 4: Light micrograph of carbon-based painted sherd with foil added to reduce charging. Rectangle defines area shown in Figure 5. Dark arrow at bottom of rectangle is tip of carbon tape to locate area of interest. Scale bar = 5 mm.

The light microscope image of the carbon-based painted sherd in Figure 4 shows the location of painted and unpainted areas. The rectangle in Figure 4 indicates the area examined by SEM-EDS mapping. The presence of potassium in the brighter yellow area of the SEM-EDS map (Figure 5) correlates well with the pigmented areas of the sherd within the rectangle in Figure 4. With these minor changes we were able to show that a SEM-EDS spectrum from within the painted area (Figure 6a) has a higher peak for potassium than does the SEM-EDS plot of the counts generated within the unpainted area (Figure 6b), indicating that potassium is more concentrated in the carbon-based pigment on the sherd.

Discussion

Stewart and Adams [1] detected twice the potassium X-ray peak intensity from the carbon-based painted section of their Ancestral Puebloan sherd compared to the non-painted area of the same sherd. Also using SEM-EDS, Striova et al. [9] detected potassium at twice the weight-percent values within carbon-based painted areas compared to unpainted areas on Ancestral Puebloan pottery. In both these studies, it was not recognized that potassium could be interpreted as a marker element for carbon-based paint.

Figures 6a and 6b of the present study also showed enhanced potassium intensity for the carbon-based painted area compared to the unpainted area of the same sherd but without carbon coating. Previous analyses indicate that the Rocky Mountain beeweed is the likely plant from which the carbon-based paint was made [5], and the extract from this plant has a high potassium concentration. Thus, we suggest here that the increased potassium X-ray signal is a marker for the presence of carbon from plant-based pigments.

Because iron was detected at similar levels in both the carbon-based painted area and unpainted area of the same sherd, it can be assumed that this iron was present primarily in the body of the sherd rather than the carbon-based paint. For the mineral-based painted sherd, potassium levels in the painted area and unpainted area of the same sherd were similar, so this potassium can be assumed to be in the body of the sherd.

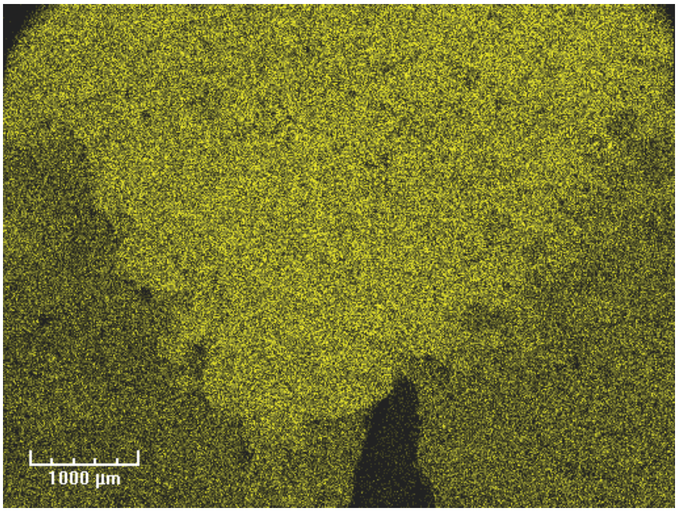

Figure 5: Potassium X-ray map showing areas of higher K content (bright yellow area). Aluminum foil surrounding the analysis area reduced specimen charging. Scale bar = 1 mm.

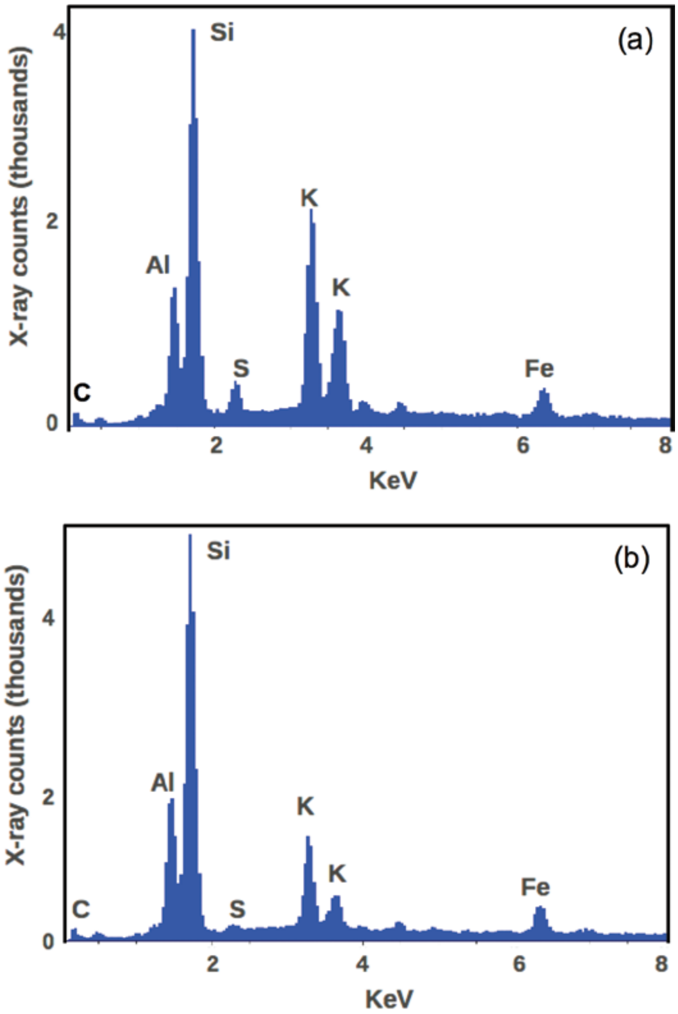

Figure 6: (a) EDS X-ray spectrum of pigmented area of carbon-based paint. (b) EDS X-ray spectrum of un-pigmented area of carbon-based paint (35 kV).

Although other researchers [10] have successfully used such techniques as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to determine elements in pottery pigments at very low elemental concentrations, LA-ICP-MS is not as generally accessible to researchers as SEM-EDS. We agree with Adams et al. [7] that SEM-EDS has the advantages of lower equipment cost and wider availability compared to other systems of element detection. By using the aluminium foil technique described in this paper, unique prehistoric pottery samples may be analysed by SEM-EDS without darkening their appearance by carbon coating.

Conclusion

We have demonstrated how the use of SEM-EDS X-ray emission spectrometry can differentiate between mineral- or carbon-based paint pigments using iron and potassium markers, respectively, on prehistoric Ancestral Puebloan pottery from the American Southwest. Specimens of pottery may be examined in the SEM-EDS without a destructive carbon coating by surrounding the area of interest with a grounded shield of aluminium foil.

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