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# Chemical Composition, Mineralogy, and Physical Structure of Pigments on Arrow and Dart Fragments from Gypsum Cave, Nevada

**JELMER W. EERKENS**
Department of Anthropology
University of California, Davis

**AMY J. GILREATH**
Far Western Anthropological Research Group
Davis, California

**BRIAN JOY** Department of
Geology University of
California, Davis

*Pigments preserved on arrow and dart weaponry fragments from Gypsum Cave, Nevada, were analyzed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), X-Ray diffraction (XRD), and electron microprobe (EM) to determine their chemical composition, mineralogy, and physical structure. Results show that a variety of minerals were used to produce the green, red, pink, brown and black pigments. Although variation in composition and mineralogy suggests some degree of experimentation, similarities in the pigments suggest the application of standardized recipes for certain colors. Pigments applied to the more ancient darts are systematically different for cane vs. wooden implements, despite the finding that cane and wooden fragments were often used as fitting parts of the same composite weapon. For example, greens applied to darts are based on malachite while greens applied to cane are based on green earth minerals. The smaller sample of arrows shows many similarities to the more ancient darts, suggesting the transmission of information about pigmenting was fairly conservative over thousands of years in the southwest Great Basin, but does not show the same wood-cane dichotomy.*

While the ethnographic record suggests pigment was widespread in the ancient Great Basin of North America, archaeological examples and studies of such pigments are relatively few. Examples of pigment are represented primarily by pictographs from rock art sites and special decorated items from well-preserved deposits. Usually these items are described and evaluated for their artistic merits; for example, the discussion may focus on how the specific colors were used within the image and on the possible emic meanings of the resulting imagery (e.g., Whitley 1998). Detailed studies of the composition of ancient pigments in the Great Basin are less common (however, see Koski et al. 1973; McKee and Thomas 1973; Whitley and Dorn 1984; further afield in California, see Backes 2004; Scott and Hyder 1993).

In the present paper we describe the physical structure, chemical composition, and mineralogy of pigments preserved on ancient hunting weaponry from Gypsum Cave, Nevada. While our goals are descriptive in nature, we consider the anthropological significance of the results as well.

## GYPSUM CAVE, NEVADA

Gypsum Cave (26CK5) is a limestone solution cave about 20 km. northwest of the Colorado River and 30 km. east of downtown Las Vegas, Nevada (Fig. 1). Mark Harrington of the Southwest Museum (in Los Angeles) directed excavations of the cave deposits in the late 1920s and early 1930s, resulting in the removal of the majority

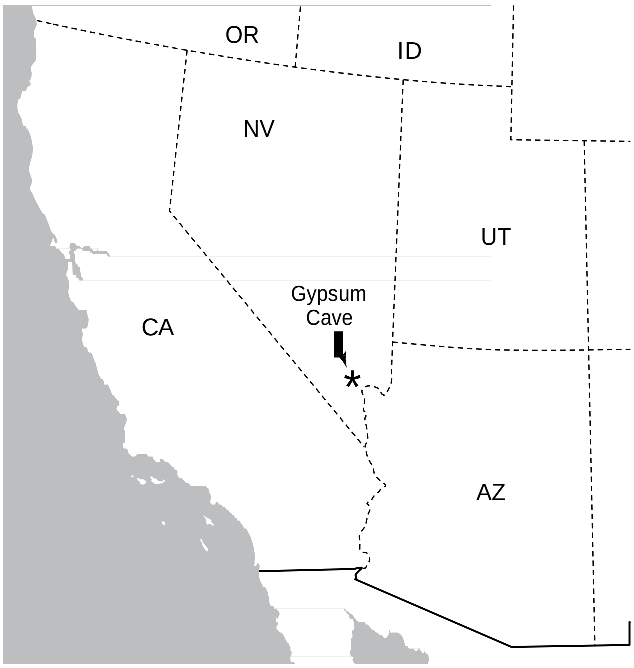


**Figure 1. Map of western United States, showing location of Gypsum Cave.**

of the sediments. Excavation methods were typical of those in practice in the early part of the twentieth century. Sediments were generally removed according to stratigraphic levels within particular rooms of the cave, but were not screened prior to disposal. Diagnostic artifacts were removed as they were encountered and bagged for transport back to the museum. The excavations produced a wide range of materials, including a robust collection of decorated and undecorated dart and arrow shaft fragments (Harrington 1933).

The cave is widely known for its well-preserved paleontological (e.g., Poinar et al. 2008) and archaeological (e.g., Harrington 1933) remains. Artifacts and ecofacts recovered from Gypsum Cave played an important role in the "early man" debates in American archaeology during the 1940s and 1950s. For example, Harrington recovered dart fragments in stratigraphic layers reported to be below layers of dung from extinct ground sloth (*Nothrotheriops shastensis*). Later radiocarbon dating of those weaponry fragments by Heizer and Berger (1970) showed them to be much younger, ca. 2,500–3,000 B.P., than the Pleistocene age suggested by their stratigraphic position relative to the sloth dung.

A limited excavation of the cave was undertaken recently by Far Western Anthropological Research Group. This work sought to expose and re-evaluate Harrington's stratigraphic levels (see Gilreath 2009); it also included recataloging and re-analysing the existing collections. That work included the pigment study reported here. We employed laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), X-Ray diffraction (XRD), and electron microprobe (EM) analyses to examine the mineralogical and structural nature of the pigmenting materials, to examine variation across different weapons types and ages, and to document variation within particular colors. In addition, a sample of items was directly dated by radiocarbon means.

## PIGMENT SAMPLE

The sample for this study consists of 33 painted weaponry fragments, listed in Table 1. The analyzed sample accounts for nearly half (46%) of all the painted dart and arrow fragments identified in the Harrington collection. Based on the presence of a nock (e.g., Fig. 2A) or other diagnostic elements, four of these artifacts were determined to represent fragments of arrows. Three (75%) were fashioned from cane (likely *Phragmites* sp.), while one was made out of wood. All four arrow fragments in this study contain only a single color, although other arrow fragments in the Gypsum Cave collection contain multiple colors on the same piece. Colors represented in the arrow sample include black and red (see Table 1). Based on their recorded stratigraphic position within the cave and associations with radiocarbon-dated items, these arrows are believed to date to between 400 and 700 years ago.

Based largely on size (i.e., diameter of 8 mm. or greater), 28 of the remaining 29 pieces were classified as dart fragments (the final sample was too small to classify into a particular weaponry category). Direct AMS dates recently obtained by Gilreath (2009) on eight of these fragments suggest that they were used between 3,200 and 3,800 radiocarbon years ago (1,370–2,340 cal B.C.); they are listed in Table 2. Only nine of the dart fragments were fashioned from cane (32%), while 19 were made out of wood. As well, over half of the dart pigment samples we analyzed display more than one color, with red and green being most common, often in combination, followed by black, brown, and pink. Decorations often consist of lines arranged in various geometric patterns,

**Table 1**

**WEAPONRY FRAGMENTS, PIGMENTS PRESENT, AND ANALYSES UNDERTAKEN IN THIS STUDY**

| | | | Colors Present | | | | | Analyses | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cat# 6F- | Weapon | Material | Rd | Gr | Bl | Br | Pi | LA-ICP-MS | XRD | EM | $^{14}$C |
| 193 | Arrow | Wood | | | x | | | x | x | | |
| 42 | Arrow | Cane | x | | | | | x | | | |
| 802 | Arrow | Cane | x | | | | | x | | | |
| 805 | Arrow | Cane | x | | | | | x | | | |
| 82B | Dart | Wood | x | x | | x | | x | | | |
| 113 | Dart | Wood | x | x | | | | x | x | x | x |
| 147 | Dart | Wood | | | x | | | x | | x | |
| 164A | Dart | Wood | x | | | | | x | | | |
| 331 | Dart | Wood | | x | | | | x | x | | |
| 428 | Dart | Wood | | x | | x | | x | x | | |
| 474 | Dart | Wood | x | | | | | x | | x | |
| 484 | Dart | Wood | x | | | | | x | | | |
| 591 | Dart | Wood | x | x | | | | x | x | x | x |
| 601A | Dart | Wood | x | | | | | x | x | x | |
| 610 | Dart | Wood | | | | x | | x | | | |
| 627 | Dart | Wood | x | | x | | | x | | | |
| 702C | Dart | Wood | x | | x | | | x | | | |
| 766A | Dart | Wood | x | | | | | x | | | |
| 929 | Dart | Wood | | | | x | | x | | | x |
| 946 | Dart | Wood | | | | x | | x | | x | |
| 993B | Dart | Wood | x | | | | | x | | | |
| 1040 | Dart | Wood | | | | x | | x | | x | x |
| 1042 | Dart | Wood | | | | x | | x | | | x |
| 241A | Dart | Cane | | | | x | | x | | | |
| 397 | Dart | Cane | | x | | | x | x | | | x |
| 398 | Dart | Cane | | x | | | | x | | | x |
| 430 | Dart | Cane | | x | | | | x | | | x |
| 480 | Dart | Cane | | x | | | x | x | | x | |
| 634B | Dart | Cane | | x | | | | x | | x | |
| 751 | Dart | Cane | x | x | | | | x | | | |
| 754 | Dart | Cane | x | | x | | | x | | x | |
| 994 | Dart | Cane | | x | | | | x | | | |
| 342A | Unkn. | Cane | x | | | | | x | | x | |

Notes: Cat#=Catalog number; Cal BP range=Calibrated age range at 2-sigma deviation. Rd=Red; Gr=Green; Bl=Black; Br=Brown; Pi=Pink.

although occasionally large sections of the shaft were homogenously covered in pigment. Figure 2F shows such a specimen with green, red, and black pigments.

We classified the pigments into five different color categories based on our subjective visual assessments. These colors include red, green, black, brown, and pink. There was some variability in these colors; for example, greens varied between deep green and pale green and browns tended to transition between true brown and a darker black-brown. Part of this variation is related to the density of the pigment itself; pigments applied in thick coatings tended to be darker than pigments that were only thinly painted on the weapon. For example, Figure 2D shows a dart fragment with brown pigments arranged in a non-linear pattern, where the color varies greatly depending on the thickness of the pigment. As an initial means to organize the analyses, the Results section below is organized according to our initial and subjective color classification.

With regard to the density of pigments, it is also relevant to note that application style varied greatly across the 33 weaponry fragments. Occasionally pigments were applied in thick coatings that clearly rested on the exterior of the original wooden or cane surface (as in both Figs. 2C and 2F). These pigments appear to have been more viscous when applied and served to completely coat the original wood or cane surface. On other specimens (as in Figs. 2D and 2E), the pigments appear to have been applied in a watery state and were absorbed *into* the cane or wood, and acted more like a dye than a paint. On such examples, the exterior surface of the wood or cane is still visible but is transformed in color. In such cases, the LA-ICP-MS analyses are likely to include a combination of both pigment and substrate, as both had to be ablated simultaneously, and it was not possible to apply XRD to these samples. Finally, in some cases it appeared that the "pigments" visible on the surface of the weapon might actually have been a precipitate leached out of string or some other substance that was originally wrapped around the surface of the item. Such pigments, then, were probably not intentionally applied but are secondary compounds that were deposited on the cane or wood surface after a more fragile material such as string decayed. We did include such apparent precipitates in the analyses below.

## METHODS

All pigment samples were analyzed using instrumentation at U.C. Davis. All 33 pigments were analyzed by LA-ICP-MS. However, due to sample quality (especially size) and instrument availability, not every sample was analyzed by


**Figure 2. Arrow (A-B) and dart (C-F) fragments with pigments from Gypsum Cave.**

**Table 2**

radiocarbon dates on Weapons from gypsum cave included in this study

| Cat # | Weapon | Material | BETA # | $\delta^{13}C/^{12}C$ | $^{14}C$ BP | Cal BP range |
|---|---|---|---|---|---|---|
| 113 | Dart | Wood | 228748 | –24.0 | 3,760 ± 50 | 3,975–4,292 |
| 591 | Dart | Wood | 228753 | –24.0 | 3,740 ± 50 | 3,929–4,243 |
| 929 | Dart | Wood | 228755 | –25.9 | 3,180 ± 50 | 3,267–3,555 |
| 1040 | Dart | Wood | 228756 | –22.0 | 3,640 ± 40 | 3,856–4,084 |
| 1042 | Dart | Wood | 228757 | –24.4 | 3,740 ± 50 | 3,929–4,243 |
| 397 | Dart | Cane | 228750 | –22.3 | 3,550 ± 40 | 3,707–3,964 |
| 398 | Dart | Cane | 228751 | –21.9 | 3,730 ± 40 | 3,934–4,230 |
| 430 | Dart | Cane | 228752 | –23.4 | 3,540 ± 40 | 3,700–3,957 |

Note: All analyses by AMS and performed by Beta Analytic. Cat# = Catalog number; Cal BP range = Calibrated age range at 2-sigma deviation. See Gilreath 2009:50–51 for additional information about these artifacts and radiocarbon results.

XRD and EM (see Table 1). Where possible, we tried to analyze at least one sample from each color group using all three techniques.

*LA-ICP-MS Methods*

The ICP-MS is an Agilent 7500a quadrupole instrument coupled to a NewWave 213 nm. laser, which was set at 20 Hz repetition rate and 25% power. For each unique pigment color on each weapon fragment, five spots approximately 160 microns in diameter were selected and ablated with the laser. Each spot was pre-ablated for five seconds to remove surface contaminants (followed by a delay to remove any geochemical "memory" of possible surface contaminants) and then ablated for 60 additional seconds. The ablated material was transported from the sample chamber by a helium carrier gas into the ICP-MS where the counts of isotopes for 26 different elements were made. For most samples we also analyzed a section of the weapon that had not been modified by the application of a pigment (again, measuring five spots). This allowed us to compare modified vs. unmodified sections and to evaluate the compositional effects of coloring.

With the exception of very small weaponry samples which were analyzed whole, small slivers of cane or wood with pigment were removed from the weapon. Slivers had to be removed to fit the specimens into the LA-ICP-MS sample chamber (~20 cm.$^2$). Slivers were attached to a glass slide with an adhesive and placed within the analysis chamber for analysis, with approximately 30–40 slivers per glass slide.

Unfortunately, it was not possible to analyze geochemically similar (i.e., matrix matched) standards, and therefore—as is common in LA-ICP-MS work—raw counts measured by the mass spectrometer could not be converted to absolute concentrations of elements (e.g., ppm. scale). Rather, we rely on the ratio of raw counts of a particular element to an internal standard, which is assumed to be constant across samples. For this study we chose potassium (K) as our internal standard. However, we also examined ratios of other elements directly to one another to characterize the pigment samples. The list of the remaining 25 elements includes common ones such as sodium (Na), calcium (Ca), and sulfur (S), metals such as iron (Fe), lead (Pb), and copper (Cu), and rare earth and high field strength elements such as molybdenum (Mo), lanthanum (La) and zirconium (Zr). Occasionally, an aberrant reading for an element was encountered in one of the five ablation spots, or after subtracting the background, a negative value resulted for an element. We removed these aberrant readings from the analysis, and averaged the remaining spots.

### *XRD Methods*

Six pigment samples were analyzed by XRD (see Table 1) to help establish mineralogy for samples analyzed by LA-ICP-MS. A larger sample would have been ideal, but in most cases there was not enough pigment material (or we felt uncomfortable removing so much pigment) to analyze by XRD. Samples were run on a Scintag XDS-20 00 diffractometer in the Materials Sciences department at U.C. Davis. Samples were scanned across 120 degrees for 40 minutes. The resulting scans were compared by computer to a large database of reference mineralogical samples (within the Materials Data Incorporated JADE® program).

### *EM Methods*

Eleven samples received EM analysis (see Table 1). Samples were mounted in epoxy and then sectioned using a Beuhler Isomet low-speed saw in such a way that the interface between cane or wood and pigment was exposed in cross section. The samples were then polished and coated with a conductive layer of carbon. EM allows us to examine the chemical composition of small sections of pigment, much smaller than the 160-micron spot size of the LA-ICP-MS. In many cases we were able to analyze individual grains within the pigment body. The numerical results, however, are more qualitative than LA-ICP-MS. In addition, EM allows us to examine the physical structure of individual pigments; i.e., whether they are coarse-grained or fine-grained, and whether particles are rounded or angular. We can also estimate the thickness of the pigment layer applied to the underlying substrate.

Mineral constituents of the pigments were analyzed using a Cameca SX100 electron microprobe located in the Department of Geology at the University of California, Davis. During analyses, accelerating potential was 15 kV, beam current was 20-30 nanoamps, and beam diameter was roughly one micron. Due to the fine mineral grain sizes and the instability of wood under the electron beam, only qualitative evaluation of mineral compositions was attempted via an examination of energy dispersive spectra (EDS). We attempted to analyze between 10 and 20 grains by EDS on each sample. In some cases, the identification of mineral species was tentative, particularly when the pigment contained a polycrystalline aggregate in which the size of some grains was less than the beam diameter. Additionally, a backscattered electron (BSE) image was produced for the section surfaces of all 11 samples.

## RESULTS

Table 3 shows the LA-ICP-MS data for the pigment and organic substrate for all samples. The most obvious signal in the data concerns the difference between the pigments and the unmodified cane or wood substrate. Figure 3 plots the first two components of a principal components analysis (PCA) on the natural log values for elements (as ratios against K). In Figure 3, each point represents a distinct pigment color or substrate from a weapon, and is the average of the five spots ablated.

The first component, which accounts for 79% of the variation in the data set, neatly separates cane and wood substrates from pigments, with four exceptions. The exceptions include a red and a green pigment (artifacts 993B and 994, respectively) that group on the edge of the substrates, and a cane and wood substrate (artifacts 430 and 766A, respectively) that group on the edge of or within the distribution of pigments. The former red and green pigments were both thinly applied on artifacts that were poorly-preserved, and did not cover the entire surface. In fact, the red was initially questioned as a true pigment, but inspection by microscope suggested it was indeed a pigment. It is possible that our five-second pre-ablation removed much of the actual pigment on these two artifacts, and that the subsequent analysis consists primarily of substrate material. On the other hand, it is unclear why the two anomalous substrates are grouping

**Table 3**

la-icp-ms data relative to k (internal standard)

| Cat# | Weapon | Color | Na | Mg | Al | S | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Cu | Zn | Rb | Sr | Y | Zr | Mo | Sn | Sb | Ba | La | Ce | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Multiplier | | | $x10^1$ | $x10^3$ | $x10^2$ | $x10^4$ | $x10^3$ | $x10^4$ | $x10^3$ | $x10^4$ | $x10^5$ | $x10^3$ | $x10^3$ | $x10^4$ | $x10^2$ | $x10^4$ | $x10^4$ | $x10^3$ | $x10^5$ | $x10^4$ | $x10^5$ | $x10^4$ | $x10^4$ | $x10^3$ | $x10^4$ | $x10^4$ | $x10^2$ |
| 994 | arrow | green | 0.88 | 0.97 | 0.09 | 2.06 | 0.12 | 0.12 | 0.34 | 0.16 | 0.36 | 0.37 | 0.92 | 0.12 | 0.06 | 0.28 | 0.73 | 0.26 | 0.03 | 0.05 | 0.03 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.03 |
| 82B | dart | green | 1.51 | 7.23 | 1.35 | 1.71 | 1.00 | 0.42 | 1.09 | 4.56 | 2.05 | 2.85 | 4.18 | 104.80 | 690.81 | 5.37 | 0.85 | 2.56 | 2.79 | 0.24 | 1.50 | 0.33 | 0.33 | 0.36 | 0.19 | 0.44 | 2.64 |
| 113 | dart | green | 1.62 | 3.07 | 1.01 | 3.25 | 0.80 | 0.42 | 1.41 | 1.45 | 1.12 | 1.70 | 1.41 | 8.69 | 313.53 | 3.79 | 0.76 | 0.82 | 1.99 | 0.20 | 1.80 | 0.78 | 0.45 | 0.86 | 0.19 | 0.34 | 1.03 |
| 331 | dart | green | 3.64 | 11.46 | 3.94 | 2.70 | 2.67 | 1.01 | 4.20 | 5.07 | 1.91 | 6.46 | 2.17 | 11.58 | 1,423.00 | 37.42 | 1.35 | 4.00 | 4.30 | 0.94 | 0.82 | 3.82 | 0.17 | 0.84 | 0.48 | 0.83 | 11.96 |
| 397 | dart | green | 0.49 | 5.45 | 1.41 | 1.90 | 1.40 | 1.59 | 1.64 | 4.10 | 0.76 | 8.37 | 6.86 | 2.45 | 0.07 | 0.36 | 5.89 | 1.60 | 1.67 | 0.55 | 0.20 | 0.03 | 0.02 | 0.11 | 0.29 | 0.52 | 0.11 |
| 398 | dart | green | 0.51 | 6.38 | 1.27 | 4.45 | 0.64 | 0.43 | 1.77 | 0.85 | 0.41 | 2.66 | 2.01 | 1.31 | 0.11 | 2.10 | 0.82 | 1.46 | 1.30 | 0.38 | 0.22 | 1.38 | 0.07 | 0.18 | 0.19 | 0.46 | 0.56 |
| 428 | dart | green | 11.60 | 35.95 | 0.92 | 1.06 | 3.87 | 0.78 | 0.35 | 4.68 | 2.09 | 7.28 | 1.31 | 344.11 | 1,203.70 | 9.66 | 0.37 | 14.22 | 4.72 | 0.11 | 0.33 | 0.14 | 0.04 | 0.14 | 0.12 | 0.41 | 1.80 |
| 430 | dart | green | 0.52 | 3.91 | 1.95 | 2.98 | 0.72 | 1.09 | 2.12 | 1.13 | 1.13 | 10.41 | 10.84 | 2.30 | 0.27 | 6.25 | 9.04 | 1.67 | 4.42 | 0.47 | 0.07 | 0.47 | 0.23 | 0.57 | 0.26 | 0.87 | 1.41 |
| 480 | dart | green | 0.19 | 3.12 | 0.96 | 3.54 | 0.54 | 0.42 | 2.01 | 0.97 | 0.49 | 1.32 | 7.14 | 1.85 | 0.27 | 1.30 | 13.06 | 0.45 | 0.79 | 0.46 | 0.05 | 0.20 | 0.03 | 0.11 | 0.13 | 0.24 | 0.27 |
| 591 | dart | green | 0.39 | 4.88 | 1.27 | 2.83 | 1.66 | 0.67 | 2.24 | 2.42 | 0.99 | 3.60 | 2.75 | 16.00 | 696.68 | 24.62 | 1.31 | 2.47 | 4.21 | 0.54 | 1.30 | 2.40 | 1.92 | 0.41 | 0.30 | 0.52 | 1.60 |
| 634B | dart | green | 0.41 | 4.05 | 2.70 | 2.29 | 1.03 | 0.88 | 10.61 | 2.46 | 1.32 | 5.64 | 9.05 | 1.39 | 0.11 | 1.53 | 3.64 | 1.28 | 2.72 | 1.37 | 0.93 | 0.39 | 0.24 | 0.25 | 0.63 | 1.07 | 0.95 |
| 751 | dart | green | 0.30 | 3.33 | 0.86 | 1.01 | 0.29 | 1.81 | 2.49 | 5.71 | 0.58 | 2.52 | 8.37 | 2.98 | 0.11 | 0.65 | 7.63 | 0.32 | 0.73 | 0.75 | 0.02 | 0.06 | 0.05 | 0.06 | 0.09 | 0.16 | 0.25 |
| 42 | arrow | red | 0.53 | 9.21 | 3.27 | 9.81 | 0.98 | 1.71 | 2.03 | 4.30 | 1.58 | 5.53 | 38.18 | 4.30 | 1.20 | 11.09 | 2.88 | 2.72 | 5.40 | 0.55 | 2.32 | 1.40 | 1.06 | 0.69 | 2.89 | 2.36 | 4.86 |
| 802 | arrow | red | 0.50 | 4.85 | 4.67 | 1.54 | 1.37 | 1.91 | 2.79 | 5.93 | 3.28 | 8.94 | 31.50 | 5.77 | 0.97 | 5.56 | 1.57 | 2.82 | 2.97 | 0.72 | 1.36 | 2.38 | 0.65 | 0.51 | 0.71 | 0.98 | 1.25 |
| 805 | arrow | red | 0.36 | 6.50 | 4.59 | 1.79 | 2.60 | 1.34 | 3.48 | 5.92 | 5.17 | 4.15 | 21.20 | 1.85 | 0.37 | 4.36 | 2.80 | 7.24 | 7.45 | 1.43 | 1.02 | 0.30 | 0.13 | 0.54 | 1.29 | 2.14 | 1.24 |
| 82B | dart | red | 0.45 | 3.28 | 2.71 | 2.11 | 0.89 | 1.81 | 1.96 | 16.16 | 2.92 | 5.76 | 65.55 | 1.85 | 17.27 | 4.34 | 1.23 | 2.02 | 22.18 | 2.02 | 1.42 | 0.53 | 4.29 | 0.75 | 1.62 | 2.10 | 3.05 |
| 113 | dart | red | 1.72 | 13.12 | 9.81 | 5.30 | 3.04 | 3.82 | 5.69 | 1.92 | 1.88 | 7.02 | 9.00 | 2.84 | 13.78 | 1.13 | 2.07 | 5.80 | 6.21 | 0.71 | 1.30 | 0.14 | 0.05 | 0.89 | 1.93 | 4.46 | 0.74 |
| 164A | dart | red | 1.32 | 7.25 | 5.13 | 5.02 | 1.14 | 1.57 | 10.37 | 1.35 | 6.26 | 5.08 | 3.86 | 3.85 | 4.49 | 211.71 | 1.30 | 4.22 | 3.86 | 3.13 | 0.17 | 7.15 | 0.41 | 2.20 | 0.35 | 0.67 | 7.01 |
| 474 | dart | red | 2.23 | 5.45 | 2.91 | 4.95 | 1.37 | 0.84 | 3.31 | 1.46 | 1.01 | 6.60 | 17.30 | 3.76 | 0.66 | 5.57 | 1.20 | 1.94 | 2.05 | 0.49 | 2.71 | 1.92 | 0.08 | 0.34 | 0.41 | 1.12 | 2.53 |
| 484 | dart | red | 0.97 | 13.75 | 6.15 | 10.79 | 3.63 | 2.50 | 9.44 | 2.98 | 5.99 | 10.98 | 6.96 | 4.90 | 7.28 | 11.71 | 3.02 | 10.99 | 7.13 | 1.36 | 0.69 | 4.43 | 0.17 | 1.55 | 1.10 | 2.86 | 2.44 |
| 591 | dart | red | 0.33 | 7.70 | 3.71 | 4.44 | 1.43 | 0.82 | 3.12 | 1.54 | 2.28 | 7.31 | 41.32 | 2.84 | 23.39 | 12.20 | 1.90 | 3.12 | 2.90 | 0.75 | 6.55 | 7.08 | 0.10 | 0.34 | 0.41 | 1.14 | 2.50 |
| 601A | dart | red | 2.99 | 10.96 | 4.79 | 1.28 | 1.42 | 1.43 | 3.88 | 3.11 | 1.21 | 8.91 | 18.42 | 2.34 | 0.32 | 2.55 | 2.56 | 2.09 | 3.29 | 1.10 | 1.06 | 0.38 | 0.05 | 0.36 | 0.50 | 1.16 | 2.11 |
| 627 | dart | red | 0.57 | 5.66 | 2.24 | 2.35 | 1.86 | 0.69 | 1.57 | 5.98 | 2.79 | 4.93 | 17.37 | 3.64 | 1.24 | 9.28 | 1.44 | 3.00 | 2.81 | 0.34 | 2.94 | 1.86 | 0.26 | 0.74 | 0.44 | 0.68 | 6.62 |
| 702C | dart | red | 1.16 | 6.81 | 3.63 | 4.35 | 2.14 | 1.65 | 4.69 | 2.42 | 1.15 | 6.90 | 30.69 | 2.36 | 1.55 | 26.66 | 2.25 | 2.95 | 4.38 | 0.72 | 1.92 | 1.35 | 3.74 | 0.48 | 0.64 | 1.49 | 4.99 |
| 751 | dart | red | 1.71 | 8.18 | 0.84 | 3.11 | 0.85 | 0.61 | 2.18 | 0.92 | 0.25 | 2.93 | 1.26 | 0.98 | 0.17 | 2.23 | 0.96 | 1.00 | 1.04 | 0.30 | 0.23 | 0.12 | 0.05 | 0.13 | 0.05 | 0.35 | 0.99 |
| 754 | dart | red | 3.00 | 9.40 | 5.88 | 7.29 | 4.89 | 2.58 | 10.63 | 5.69 | 6.07 | 15.70 | 6.14 | 7.29 | 4.19 | 11.89 | 8.27 | 4.62 | 6.13 | 1.68 | 0.30 | 1.35 | 0.35 | 2.18 | 1.02 | 2.10 | 4.73 |
| 766A | dart | red | 3.40 | 10.11 | 10.34 | 5.14 | 6.75 | 3.34 | 14.90 | 5.45 | 5.63 | 8.61 | 39.06 | 5.45 | 3.02 | 3.82 | 5.00 | 19.20 | 8.88 | 1.50 | 5.26 | 0.99 | 1.81 | 2.75 | 1.53 | 3.43 | 4.13 |
| 993B | dart | red | 4.05 | 41.64 | 0.32 | 0.92 | 0.41 | 0.06 | 0.17 | 0.20 | 0.20 | 0.60 | 0.16 | 0.62 | 0.04 | 0.90 | 0.25 | 1.61 | 0.30 | 0.03 | 0.76 | 0.02 | 0.00 | 0.03 | 0.03 | 0.10 | 0.13 |
| 342A | unk. | red | 0.44 | 6.08 | 2.79 | 4.33 | 1.78 | 0.96 | 2.81 | 13.79 | 2.85 | 4.67 | 103.90 | 8.50 | 0.42 | 3.94 | 2.07 | 4.46 | 2.17 | 0.80 | 1.68 | 0.12 | 1.21 | 4.77 | 0.36 | 0.65 | 0.79 |
| 397 | dart | pink | 1.35 | 3.55 | 4.15 | 3.32 | 1.30 | 1.17 | 2.56 | 1.51 | 0.54 | 5.85 | 14.38 | 1.13 | 0.09 | 0.37 | 2.30 | 2.98 | 2.81 | 1.21 | 0.74 | 0.07 | 0.07 | 0.51 | 0.52 | 1.04 | 0.37 |
| 480 | dart | pink | 0.65 | 3.50 | 7.99 | 4.99 | 1.03 | 4.53 | 7.50 | 1.42 | 0.54 | 4.42 | 12.40 | 12.04 | 34.50 | 4.03 | 10.83 | 1.15 | 19.76 | 33.89 | 3.59 | 1.44 | 1.53 | 0.55 | 0.37 | 1.15 | 1.92 |
| 241A | arrow | brown | 0.55 | 5.47 | 2.59 | 2.90 | 1.27 | 0.80 | 1.93 | 1.01 | 1.07 | 3.97 | 1.85 | 1.52 | 0.18 | 1.81 | 1.11 | 2.22 | 2.94 | 0.76 | 0.12 | 0.26 | 0.02 | 0.33 | 0.31 | 0.80 | 0.34 |
| 82B | dart | brown | 0.84 | 3.53 | 2.43 | 2.40 | 0.86 | 1.43 | 5.37 | 11.32 | 2.01 | 6.30 | 43.24 | 2.82 | 19.10 | 9.88 | 1.34 | 2.09 | 18.78 | 3.36 | 0.83 | 0.96 | 3.30 | 1.25 | 1.19 | 1.27 | 1.99 |
| 428 | dart | brown | 2.15 | 10.05 | 3.19 | 5.51 | 3.69 | 1.31 | 3.92 | 2.78 | 2.12 | 6.56 | 4.41 | 11.19 | 45.40 | 13.40 | 2.32 | 5.05 | 4.86 | 0.60 | 0.27 | 8.52 | 0.11 | 1.25 | 0.78 | 1.15 | 7.09 |
| 610 | dart | brown | 0.35 | 8.69 | 6.89 | 1.81 | 1.91 | 1.57 | 3.63 | 1.80 | 1.34 | 5.22 | 4.27 | 1.90 | 0.34 | 4.98 | 3.85 | 2.95 | 7.21 | 0.85 | 0.14 | 0.34 | 0.07 | 0.49 | 0.60 | 1.55 | 0.66 |
| 929 | dart | brown | 0.11 | 4.62 | 0.72 | 11.72 | 2.07 | 0.20 | 0.53 | 0.30 | 1.20 | 1.04 | 0.78 | 0.68 | 0.50 | 3.62 | 0.52 | 5.85 | 0.49 | 0.08 | 0.06 | 17.75 | 0.05 | 0.16 | 0.09 | 0.20 | 0.48 |

## Table 3 (Continued)

la-icp-ms data relative to k (internal standard)

| Cat# | Weapon | Color | Na | Mg | Al | S | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Cu | Zn | Rb | Sr | Y | Zr | Mo | Sn | Sb | Ba | La | Ce | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Multiplier | | | $x10^1$ | $x10^3$ | $x10^2$ | $x10^4$ | $x10^3$ | $x10^4$ | $x10^3$ | $x10^4$ | $x10^5$ | $x10^3$ | $x10^3$ | $x10^4$ | $x10^2$ | $x10^4$ | $x10^4$ | $x10^3$ | $x10^5$ | $x10^4$ | $x10^5$ | $x10^4$ | $x10^4$ | $x10^3$ | $x10^4$ | $x10^4$ | $x10^2$ |
| 946 | dart | brown | 0.51 | 19.80 | 4.92 | 3.65 | 1.97 | 1.43 | 3.57 | 2.27 | 1.44 | 12.67 | 10.65 | 2.35 | 0.38 | 8.46 | 2.54 | 4.00 | 3.26 | 0.65 | 0.57 | 43.92 | 0.04 | 0.86 | 0.54 | 1.48 | 1.95 |
| 1040 | dart | brown | 2.16 | 7.57 | 6.04 | 7.08 | 2.58 | 2.71 | 9.28 | 3.34 | 3.90 | 9.52 | 20.55 | 5.85 | 1.58 | 37.02 | 6.40 | 7.67 | 6.29 | 1.16 | 0.63 | 406.50 | 1.59 | 2.54 | 1.32 | 4.24 | 4.73 |
| 1042 | dart | brown | 1.47 | 16.57 | 13.64 | 5.98 | 3.99 | 2.76 | 13.08 | 6.29 | 5.52 | 25.84 | 11.48 | 9.50 | 4.66 | 11.80 | 8.56 | 6.51 | 9.65 | 1.04 | 0.65 | 6.18 | 0.81 | 3.20 | 1.65 | 3.66 | 4.81 |
| 147 | dart | black | 2.21 | 7.20 | 5.65 | 7.82 | 2.25 | 1.72 | 3.96 | 2.71 | 3.94 | 8.17 | 5.05 | 4.92 | 39.91 | 41.44 | 3.83 | 3.87 | 5.27 | 1.69 | 0.44 | 5.71 | 0.35 | 0.62 | 1.16 | 2.20 | 34.94 |
| 193 | arrow | black | 2.06 | 3.98 | 1.26 | 3.55 | 0.81 | 0.45 | 2.83 | 1.51 | 0.10 | 388.2 | 1.65 | 1.39 | 1.24 | 1.27 | 1.05 | 3.78 | 1.68 | 0.25 | 2.06 | 0.06 | 0.04 | 1.58 | 0.26 | 0.50 | 14.82 |
| 627 | dart | black | 0.69 | 5.06 | 0.92 | 3.06 | 1.52 | 0.30 | 0.81 | 0.77 | 2.06 | 3.30 | 4.86 | 1.10 | 0.65 | 3.89 | 1.05 | 3.05 | 0.83 | 0.19 | 0.50 | 2.33 | 0.11 | 0.28 | 0.14 | 0.44 | 2.09 |
| 702C | dart | black | 1.05 | 9.62 | 2.55 | 5.06 | 1.12 | 0.67 | 1.69 | 0.94 | 0.67 | 3.55 | 4.44 | 1.65 | 51.25 | 2.72 | 1.31 | 2.10 | 2.60 | 0.34 | 0.64 | 0.14 | 0.04 | 0.27 | 0.32 | 0.68 | 0.34 |
| 754 | dart | black | 1.35 | 4.88 | 3.08 | 9.31 | 2.24 | 2.04 | 3.35 | 1.75 | 0.88 | 4.66 | 10.20 | 1.88 | 0.19 | 2.73 | 6.62 | 4.95 | 3.80 | 0.73 | 0.43 | 0.33 | 0.29 | 0.62 | 0.45 | 1.09 | 0.87 |
| 42 | arrow | cane | 0.77 | 2.87 | 0.01 | 0.88 | 0.10 | 0.01 | 0.02 | 0.04 | 0.25 | 0.23 | 0.03 | 0.12 | 0.03 | 0.14 | 0.96 | 0.43 | 0.05 | 0.01 | 0.58 | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.02 |
| 193 | arrow | wood | 1.33 | 0.58 | 0.02 | 1.19 | 0.02 | 0.01 | 0.02 | 0.01 | 0.14 | 0.62 | 0.02 | 0.03 | 0.03 | 0.11 | 0.35 | 0.22 | 0.01 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 |
| 241 | arrow | cane | 0.24 | 0.12 | 0.00 | 0.22 | 0.01 | 0.00 | 0.00 | 0.00 | 0.06 | 0.35 | 0.00 | 0.03 | 0.01 | 0.03 | 0.37 | 0.03 | 0.00 | 0.00 | 0.11 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 802 | arrow | cane | 0.24 | 1.41 | 0.01 | 0.26 | 0.05 | 0.02 | 0.39 | 0.01 | 0.23 | 0.25 | 0.01 | 0.02 | 0.04 | 0.32 | 0.68 | 0.11 | 0.00 | 0.09 | 0.04 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| 805 | arrow | cane | 0.45 | 0.33 | 0.00 | 0.44 | 0.01 | 0.01 | 0.00 | 0.01 | 0.14 | 0.08 | 0.00 | 0.08 | 0.02 | 0.12 | 0.48 | 0.04 | 0.01 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 994 | arrow | cane | 1.05 | 0.97 | 0.00 | 0.37 | 0.17 | 0.00 | 0.02 | 0.01 | 0.66 | 0.35 | 0.02 | 0.03 | 0.00 | 0.01 | 0.44 | 0.42 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.12 | 0.00 | 0.00 | 0.00 |
| 82B | dart | wood | 0.83 | 1.03 | 0.00 | 0.70 | 0.11 | 0.01 | 0.02 | 0.00 | 0.27 | 0.27 | 0.02 | 0.07 | 0.27 | 0.57 | 0.28 | 1.23 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 |
| 113 | dart | wood | 4.60 | 3.82 | 0.11 | 1.19 | 0.28 | 0.06 | 0.09 | 0.04 | 0.32 | 0.98 | 0.16 | 0.21 | 2.23 | 2.95 | 0.45 | 0.81 | 0.08 | 0.01 | 0.08 | 0.03 | 0.01 | 0.05 | 0.05 | 0.04 | 0.08 |
| 147 | dart | wood | 1.68 | 0.82 | 0.00 | 0.60 | 0.20 | 0.01 | 0.00 | 0.00 | 0.41 | 0.63 | 0.00 | 0.06 | 0.02 | 0.18 | 0.35 | 1.19 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 164A | dart | wood | 2.22 | 1.12 | 0.02 | 0.72 | 0.18 | 0.03 | 0.40 | 0.01 | 0.28 | 0.36 | 0.04 | 0.05 | 0.08 | 2.62 | 0.26 | 0.91 | 0.10 | 0.07 | 0.01 | 0.09 | 0.00 | 0.01 | 0.01 | 0.01 | 0.31 |
| 331 | dart | wood | 9.37 | 1.26 | 0.02 | 0.37 | 0.20 | 0.01 | 0.17 | 0.00 | 0.27 | 0.15 | 0.04 | 0.02 | 0.21 | 0.45 | 0.21 | 0.62 | 0.01 | 0.02 | 0.00 | 0.03 | 0.00 | 0.03 | 0.00 | 0.00 | 0.05 |
| 397 | dart | cane | 4.46 | 1.02 | 0.01 | 1.40 | 0.07 | 0.01 | 0.01 | 0.00 | 0.19 | 0.53 | 0.03 | 0.03 | 0.02 | 0.12 | 0.20 | 0.33 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 |
| 398 | dart | cane | 5.52 | 0.82 | 0.05 | 1.14 | 0.08 | 0.03 | 0.08 | 0.03 | 0.39 | 2.34 | 0.09 | 0.12 | 0.04 | 0.34 | 0.89 | 0.17 | 0.10 | 0.03 | 0.09 | 0.01 | 0.00 | 0.05 | 0.01 | 0.03 | 0.02 |
| 430 | dart | cane | 13.24 | 10.69 | 5.54 | 5.62 | 4.51 | 2.11 | 10.75 | 5.00 | 1.67 | 20.15 | 8.39 | 16.33 | 0.54 | 4.53 | 3.83 | 7.29 | 6.55 | 6.91 | 0.55 | 1.80 | 0.06 | 0.81 | 1.04 | 2.39 | 3.11 |
| 480 | dart | cane | 1.26 | 2.39 | 0.00 | 0.35 | 0.14 | 0.00 | 0.03 | 0.01 | 0.34 | 0.87 | 0.02 | 0.01 | 0.02 | 0.16 | 0.61 | 0.50 | 0.01 | 0.01 | 0.02 | 0.00 | 0.00 | 0.14 | 0.00 | 0.00 | 0.00 |
| 484 | dart | wood | 4.58 | 0.37 | 0.01 | 0.30 | 0.08 | 0.00 | 0.06 | 0.00 | 0.12 | 0.25 | 0.01 | 0.05 | 0.06 | 0.22 | 0.17 | 0.28 | 0.01 | 0.02 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 | 0.00 | 0.03 |
| 601A | dart | wood | 6.51 | 0.70 | 0.01 | 0.53 | 0.17 | 0.04 | 0.13 | 0.01 | 0.53 | 0.25 | 0.03 | 0.07 | 0.07 | 0.22 | 0.24 | 0.72 | 0.01 | 0.02 | 0.00 | 0.01 | 0.00 | 0.03 | 0.00 | 0.00 | 0.02 |
| 610 | dart | wood | 0.86 | 1.86 | 0.26 | 2.29 | 0.33 | 0.10 | 0.15 | 0.14 | 0.30 | 1.05 | 0.22 | 0.28 | 0.03 | 0.24 | 0.62 | 0.59 | 0.33 | 0.04 | 0.09 | 0.01 | 0.01 | 0.80 | 0.05 | 0.07 | 0.08 |
| 627 | dart | wood | 0.35 | 0.59 | 0.05 | 1.41 | 0.23 | 0.00 | 0.06 | 0.16 | 0.81 | 0.61 | 1.07 | 0.30 | 0.22 | 0.54 | 0.78 | 1.01 | 0.20 | 0.00 | 0.27 | 0.00 | 0.03 | 0.03 | 0.11 | 0.08 | 0.12 |
| 634B | dart | cane | 3.16 | 2.67 | 0.40 | 0.86 | 0.28 | 0.18 | 1.91 | 0.48 | 0.88 | 1.23 | 1.77 | 0.24 | 0.04 | 0.58 | 1.22 | 0.44 | 0.47 | 0.23 | 0.06 | 0.17 | 0.10 | 0.09 | 0.06 | 0.22 | 0.22 |
| 702C | dart | wood | 2.18 | 1.21 | 0.00 | 0.28 | 0.16 | 0.01 | 0.00 | 0.00 | 0.26 | 0.23 | 0.01 | 0.03 | 0.02 | 0.48 | 0.68 | 0.58 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.07 | 0.00 | 0.00 | 0.08 |
| 766A | dart | wood | 11.18 | 7.47 | 0.31 | 9.96 | 7.28 | 0.21 | 0.31 | 0.94 | 0.59 | 6.53 | 0.28 | 3.71 | 5.30 | 0.46 | 0.27 | 13.29 | 1.64 | 0.35 | 2.98 | 0.00 | 0.00 | 0.10 | 0.15 | 0.69 | 0.02 |
| 929 | dart | wood | 0.18 | 1.20 | 0.00 | 0.21 | 0.16 | 0.00 | 0.00 | 0.00 | 0.06 | 0.03 | 0.00 | 0.00 | 0.01 | 0.02 | 0.27 | 0.19 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| 993B | dart | wood | 3.44 | 14.00 | 0.03 | 0.75 | 0.41 | 0.06 | 0.17 | 0.20 | 0.20 | 0.60 | 0.16 | 0.62 | 0.04 | 0.90 | 0.25 | 1.61 | 0.30 | 0.03 | 0.76 | 0.02 | 0.00 | 0.03 | 0.03 | 0.10 | 0.13 |
| 1040 | dart | wood | 22.83 | 2.90 | 0.03 | 1.58 | 0.46 | 0.01 | 0.06 | 0.03 | 0.80 | 0.31 | 0.02 | 0.53 | 0.15 | 0.98 | 0.17 | 1.25 | 0.01 | 0.02 | 0.01 | 0.02 | 0.00 | 0.05 | 0.00 | 0.00 | 0.17 |
| 342A | unk. | cane | 0.49 | 1.70 | 0.02 | 0.45 | 0.91 | 0.03 | 14.30 | 0.07 | 0.13 | 0.81 | 0.11 | 0.22 | 0.07 | 0.61 | 1.93 | 1.00 | 0.14 | 0.11 | 0.23 | 0.02 | 0.00 | 0.04 | 0.03 | 0.05 | 0.02 |

Notes: unk. = unknown. "Multiplier" indicates the number that the reported ratio in the table should be multiplied by to arrive at the true ratio of that element against K.

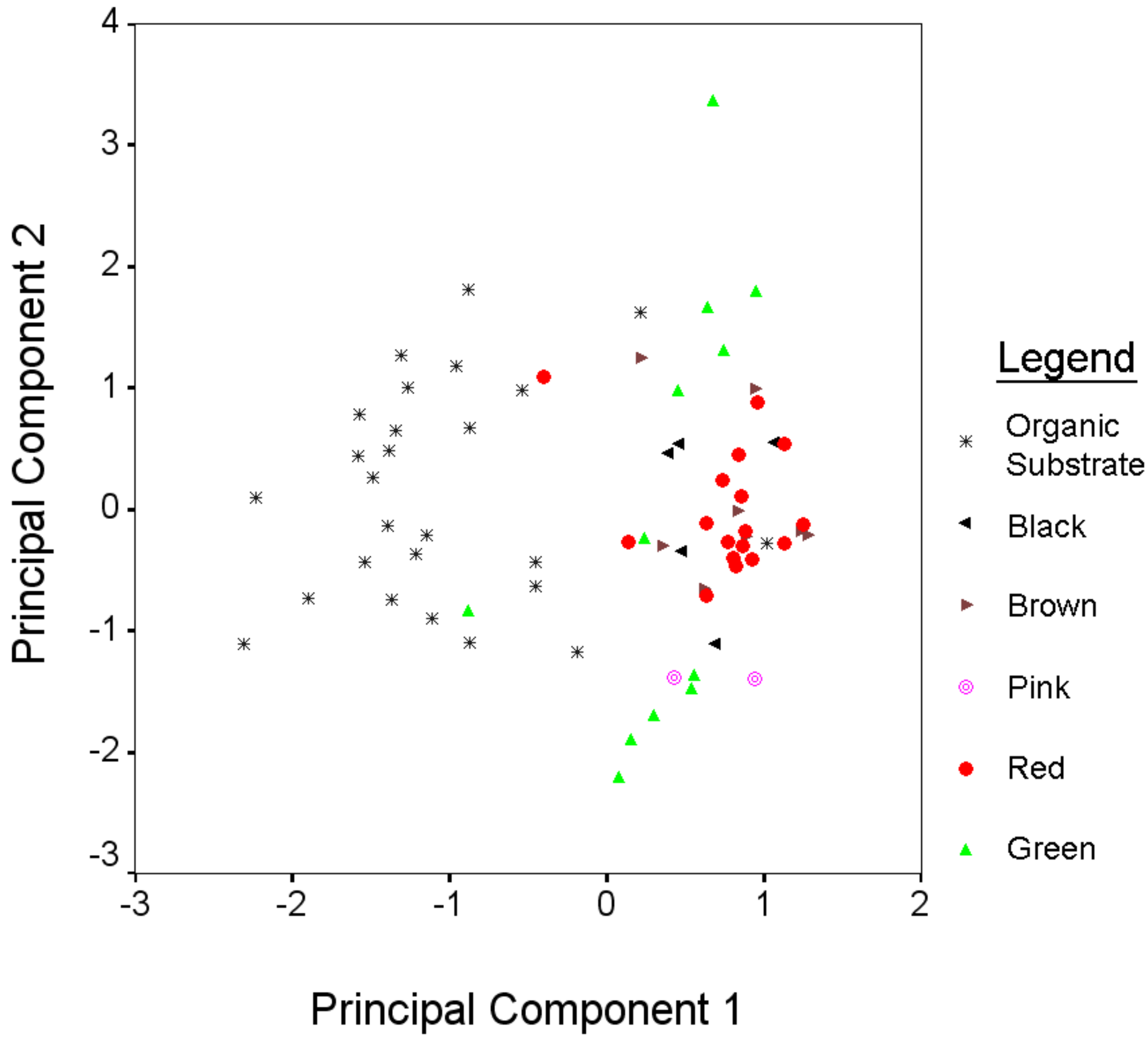


**Figure 3. PCA of LA-ICP-MS data, showing separation of wood and cane substrates versus pigments.**

with the pigments. One possibility is that pigments on these artifacts penetrated more deeply into the organic substrate, although there is no obvious discoloration to the wood and cane substrate in these cases.

Relative to K, Na was the only element that was consistently higher in the unmodified cane or wood. Most other elements were present in much higher abundance in the pigments than in the organic substrate (up to 10,000 times higher in some cases), particularly transition (Cu, Fe, Mn, Zn) and other metals (Al, Sn, Pb). Indeed, a bivariate plot of almost any of these elements produces essentially the same plot as that from the PCA, with the cane and wood substrates falling well below the pigments. This suggests that many of the pigments derive from metal-bearing minerals and that those minerals did not contain Na as a major constituent. On the other hand, there is some overlap between organic substrates and pigments for some of the alkaline earth metals and some non-metals (e.g., S, Mg, and Ba), especially for green pigments. There are no obvious elemental differences between the cane and wood substrates. Importantly, these analyses show the geochemical signature for an organic substrate relative to a pigment.

It is possible that LA-ICP-MS analyses on some of the pigments included a small component of organic substrate as part of the ablation process. This may be especially true for thin pigment washes where the pigment may have penetrated the substrate, as discussed above for artifacts 430 and 766A. EM images for 11 artifacts do not suggest such penetration was extensive. However, by focusing our subsequent pigment analyses on the ratios of elements that are extremely low in the substrates, we can minimize the potential effects of any substrate interaction. Having separated organic substrates from pigments, we now focus our attention on the pigments only. The sections below summarize the significant findings by color.

For samples examined by EM, Table 4 characterizes pigments based on their physical appearances in BSE images as either coarse-, medium- or fine-grained. We measured the maximum diameter of grains within the pigment as well. Table 4 also reports tentative mineralogy based on EDS analyses on particular grains within the pigment matrix, showing the more common constituents.

*Green*

Green has the most striking elemental distinctions of the analyzed pigment colors. In total, we analyzed 12 artifacts with green pigment: seven cane and five wood darts (no arrows). Four of these were also subjected to XRD and four to EM analysis (two of the four received both analyses). Figure 4 plots Cu/K and Rb/Sc, highlighting

**Table 4**

pigment texture and mineralogy as reconstructed from em bse images and eds analyses of particular spots

| Cat # | Color | Texture | Max. Diam. | Reconstructed Mineralogy based on EDS |
|---|---|---|---|---|
| 113 | Green | Coarse | 75 | Malachite, Plagioclase, Alkali Feldspar, Calcite, Apatite |
| 147 | Black | Coarse | 60 | Cu-Sulfate, Cuprite, Quartz, Alumina-Silicate |
| 474 | Red | Fine | <5 | n/a |
| 591 | Green | Coarse | 80 | Malachite, Dolomite, Quartz, Plagioclase |
| 591 | Red | Coarse | 40 | Hematite, Cuprite |
| 601A | Red | Fine | <5 | Iron oxide, Al-Na Rich Silicate |
| 946 | Brown | Fine | 5 | Iron oxide, Silicate, Carbonate |
| 1040 | Brown | Medium | 25 | Fe Rich Alumina-Silicate |
| 480 | Green | Fine | 10 | Fe-K-Na-Mg-Ca Rich Alumina-Silicate, Quartz |
| 634B | Green | Fine | <5 | Fe-K-Na-Mg-Ca Rich Alumina-Silicate, Quartz |
| 754 | Black | Fine | <5 | Fe-K Rich Silicate, Plagioclase, Alkali Feldspar |
| 342A | Red | Fine | 10 | Iron oxide, Quartz, Alumina-Silicate |

Notes: Cat # = Catalog number; Max. Diam. = Maximum observed diameter of inclusions within pigment; Apparent Mineralogy = Interpretation of mineralogy, in decreasing order of importance within pigment. For artifact 474 we did not perform EDS.

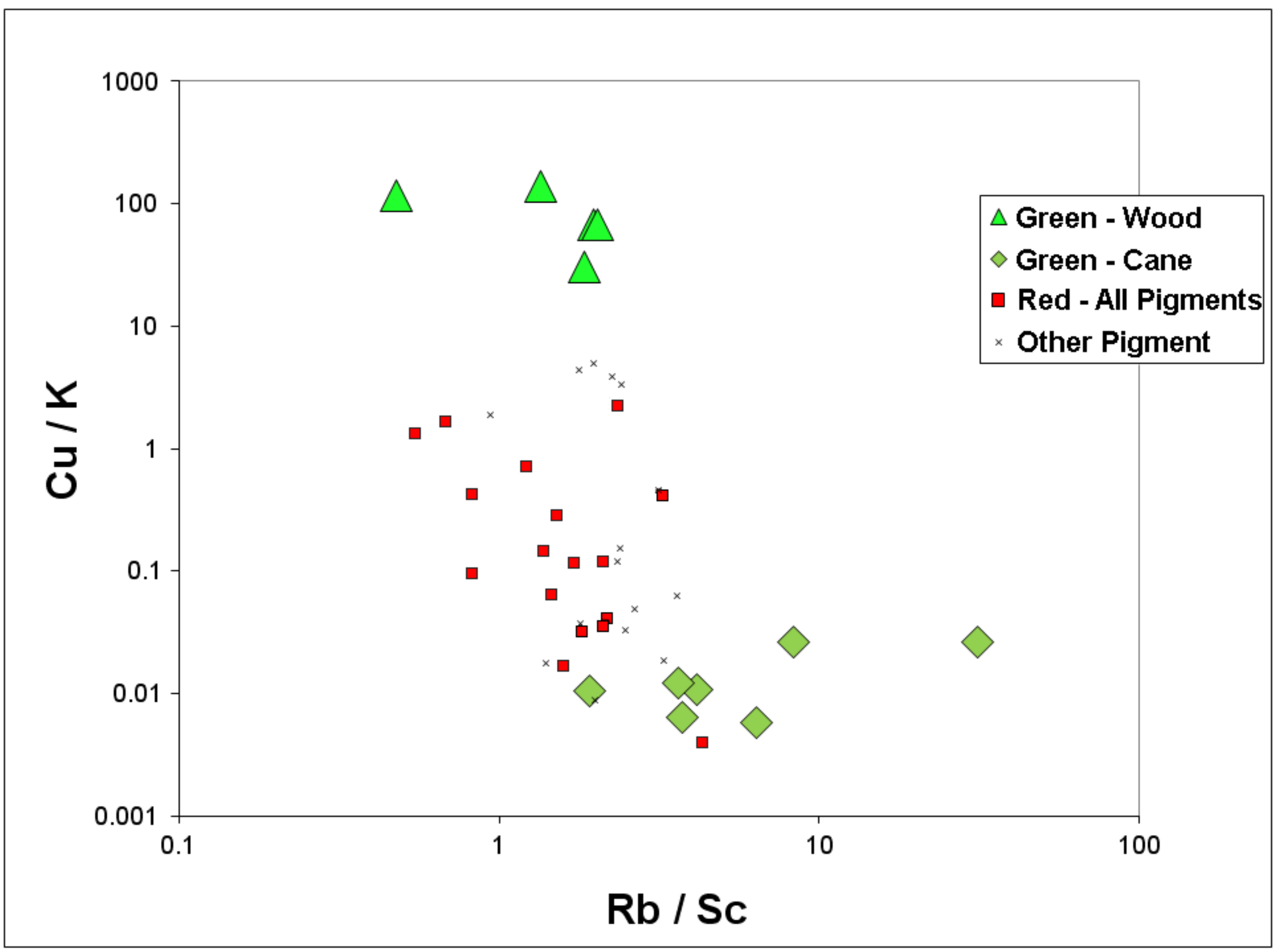


**Figure 4. Relative abundances of Cu and Ti (LA-ICP-MS analysis) showing two groups of greens.**

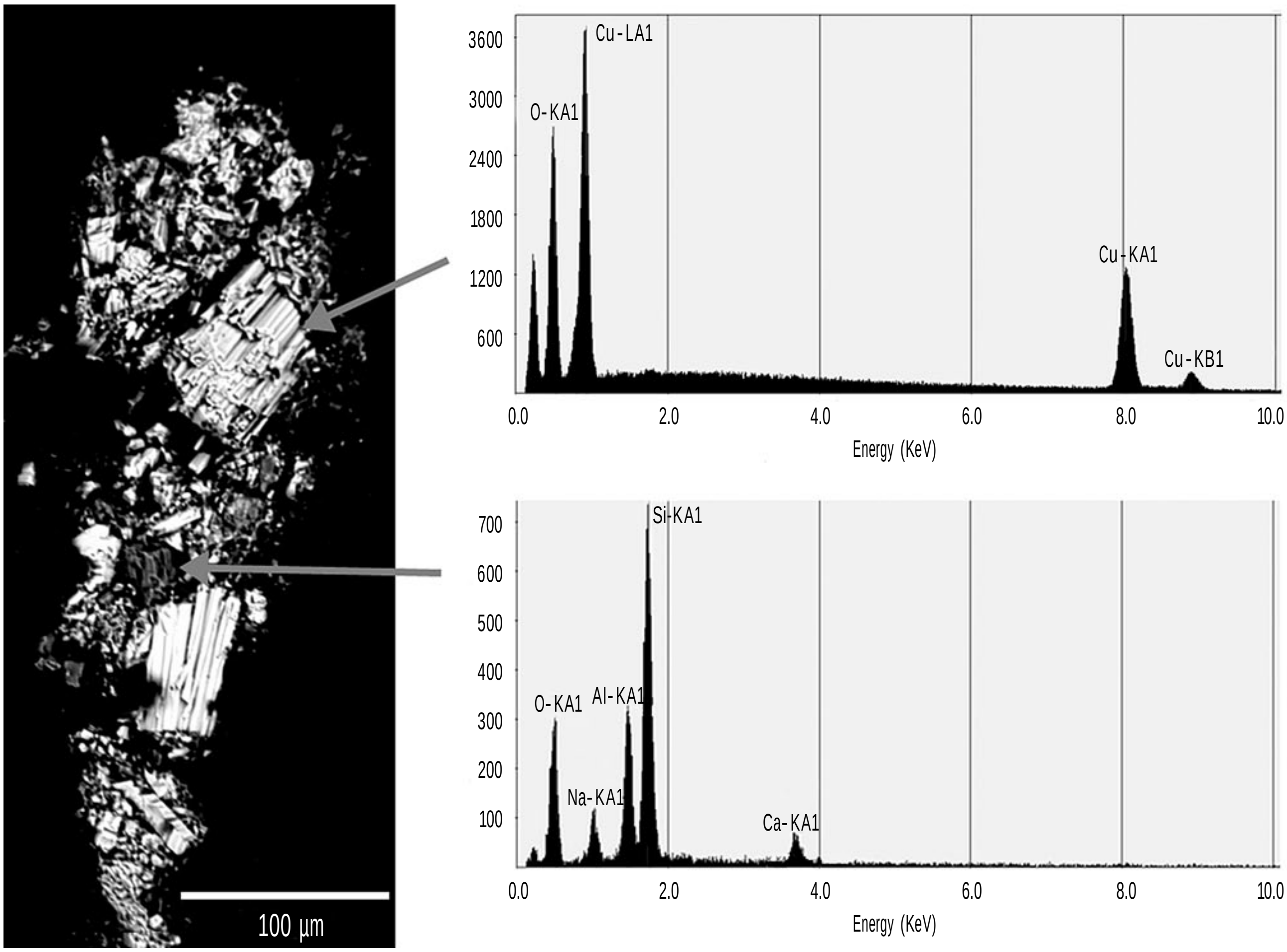


**Figure 5. BSE image of sample 113 and associated EDS scans at two locations. Note cleavage and fracturing pattern of the upper copper-rich mineral, consistent with malachite. We interpret the lower mineral as plagioclase feldspar.**

green colors versus other pigments. As seen, green pigments clearly divide into two groups, a high-Cu group and a low-Cu group. Copper comprises between 75% and 90% of the ICP-MS element raw counts for the high Cu group, and is 10 to 10,000 times higher than in other samples. These pigments are displayed as triangles in the upper part of Figure 4 and are notably elevated in Na, Co, Pb, and Zn as well.

Interestingly, this division into high and low Cu also neatly divides the sample by substrate type. All greens on wood implements belong to the high-Cu group, with Cu levels nearly 1,000 times higher than in the low-Cu group, which are all on cane and are plotted as diamonds in the lower part of the graph. These greens on cane have even lower Cu values than other pigments. A compositional difference between pigments used on wooden versus cane darts is a trend that repeats in other colors.

XRD and EM-EDS analyses on two high-Cu pigments indicate that the copper-bearing mineral is malachite ($Cu_2[(OH)_2|CO_3]$). For example, Figure 5 shows a back-scattered electron (BSE) scan of a small section of the green pigment on artifact 113, with insets showing EM-EDS analyses at two spots. Contrast is increased to highlight the physical structure of the pigment. The organic substrate lies on the left side of the pigment, but is not visible due to low brightness. The upper EDS scan shows our analysis of a copper-rich inclusion in the pigment, with peaks for copper, oxygen and carbon, consistent with the chemistry of malachite. Cleavage and fracturing patterns are also similar to a malachite standard we examined by EM. The lower EDS spectrum represents a mineral that is completely embedded within the malachite and displays lower brightness, and hence, includes elements with

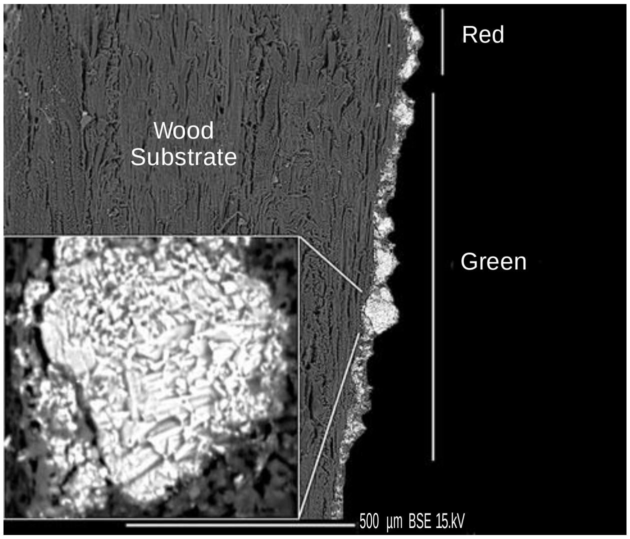


**Figure 6. BSE image of sample 591 showing green malachite-based pigment; inset shows large aggregate of malachite grains. Note coarse-grained nature of pigment layer.**

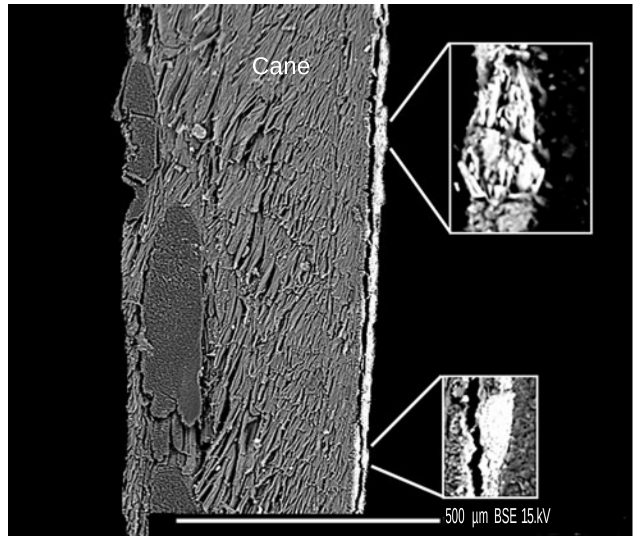


**Figure 7. BSE image of non-cuprous green, with insets of hornblende (upper) and celadonite (lower) grains (sample 480).**

lower atomic number than the malachite. Relative peak heights for Na, Ca, Al, Si, and O suggest the presence of plagioclase feldspar. Summing the bright pixels within the pigment, we estimate that over 65% of this pigment is made up of malachite. Malachite was used widely as a source of green pigment by artisans around the globe, including in California and Nevada (Campbell 2007:44).

Figure 6 shows a BSE image of the green from sample 591. The woody structure of the weapon appears on the left side of the image, while the pigment appears as the brighter vertical line through the center. The inset is zoomed in on one of the larger aggregates of malachite grains. The BSE images reveals poorly sorted and sub-rounded to sub-angular grains with a maximum diameter of over 50 microns; it is thus a very coarse pigment. The thickness of the pigment across the wooden substrate is also highly variable. For this artifact, XRD and EM-EDS analysis revealed the presence of malachite, with minor amounts of quartz ($SiO_2$), calcite ($CaCO_3$), gypsum ($Ca[SO_4]\ 2H_2O$), and apatite ($Ca_5(PO_4)_3(F,Cl,OH)$), as well as alkali ($(K,Na)AlSi_3O_8$) and plagioclase ($(Na,Ca)(Al,Si)_4O_8$) feldspars. As discussed below, these minerals are present within some, but not all, of the other pigments. It is unclear if they were intentionally added or not (as, for example, a component in an extender or inorganic clay-based binder). Alternatively, they may be contaminants (as, for example, naturally-occurring minerals within the cave sediments). EM images show these minerals are often deep within the pigment, suggesting the former.

The non-cuprous green pigments on cane implements have a very different composition and structure (Fig. 7). These greens are lighter in color, unlike the darker and more vibrant greens produced by the malachite-based pigments. EM-BSE images show the pigments to be much finer-grained, with maximum particle size under 15 microns, and they were applied more evenly in thickness across the cane surface. LA-ICP-MS data indicate that relative to the other pigments, these greens have elevated levels of Na, Fe, and Rb. EM-EDS data suggest that the major mineral in these pigments is a green earth (or *terre verte*), likely either glauconite ($(K, Na)(Fe, Al, Mg)(Al,Si)Si_3O_{10}\bullet(OH)_2$) or celadonite ($K(Mg,Fe^{2+})(Fe^{3+},Al)(Si_4O_{10}\bullet(OH)_2)$). Glauconite is a soft green mineral characteristic of marine depositional environments of the continental shelf (Rieder et al. 1998), and has been reported as being present in deposits less than 10 km. to the west of Gypsum Cave (Rowland et al. 1990), while celadonite is typically associated with altered basalts, and is also available in southern Nevada. Compositionally, these two minerals are similar. Green earth is reported as a green pigmenting agent in California (Campbell 2007; Scott et al. 2002) and elsewhere (e.g., Wainwright et al. 2009). EM-EDS data also indicate the presence of quartz, hornblende, alkali feldspars, and possibly clay

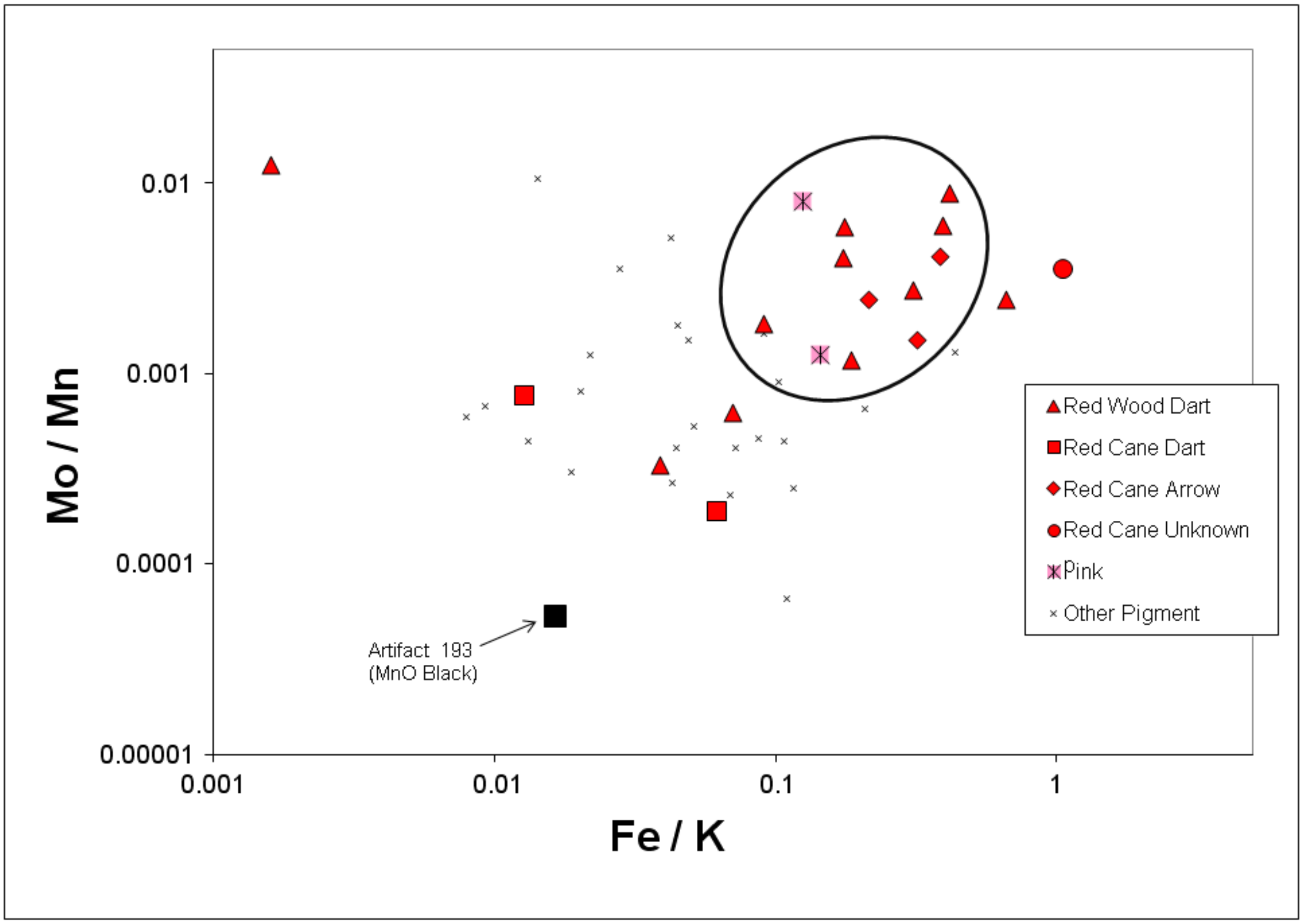


**Figure 8. Relative abundances of Fe and Rb/Sr (LA-ICP-MS analysis) highlighting groups of red and pink pigments.**

minerals within this matrix, but not the presence of calcite, gypsum, or apatite, as in the cuprous greens.

*Red*

Red pigments from 17 samples were analyzed by LA-ICP-MS, including three cane arrows, two cane darts, one cane artifact of unknown weaponry type, and eleven wooden darts. Three of these were also subjected to both XRD and EM analyses, while three others received only EM analysis. As shown in Figure 8, the majority of the red pigments tend to have higher levels of Fe, and in artifacts with the highest values, accounts for 25–75% of the raw LA-ICP-MS counts. Red pigments also have elevated levels of Mo, which, although at concentrations about 4-5 magnitudes lower, covaries strongly with Fe in the red pigments.

XRD analysis on two of the high-iron pigments (591 and 601A) indicates large quantities of hematite ($Fe_2O_3$); again, a common component of red pigments worldwide (e.g., Bordignon et al. 2007; Clottes 1993; Hernanz et al. 2008), including in western North America (Scott and Hyder 1993; Striova et al. 2006; Wallace 1947). The XRD scans also indicate the presence of minor quantities of quartz, calcite, dolomite ($CaMg(CO_3)_2$), ankerite ($CaFe(CO_3)_2$), and a trace of gypsum. EM-EDS analysis of one of these two specimens (601A) and another high-Fe red (342A) corroborates the XRD results. Based on these results and similar overall geochemistry, we believe that most of the reds can be grouped into a single pigment recipe based on hematite, with additional minerals either naturally co-occurring within the hematite source, intentionally added, or incorporated post-depositionally (i.e., contamination from surrounding soil or formed by chemical alteration of the original pigments). We have highlighted this group with an overlying ellipse (not calculated statistically, but merely to draw attention to the association). The two pink pigments also fall into this general ellipse based on Fe and Mo, but are different in other ways (see below).

Five red pigments do *not* fall into the high Fe and Mo category, including three wooden darts and all cane darts. One of these wood dart samples (993B) is isolated in the

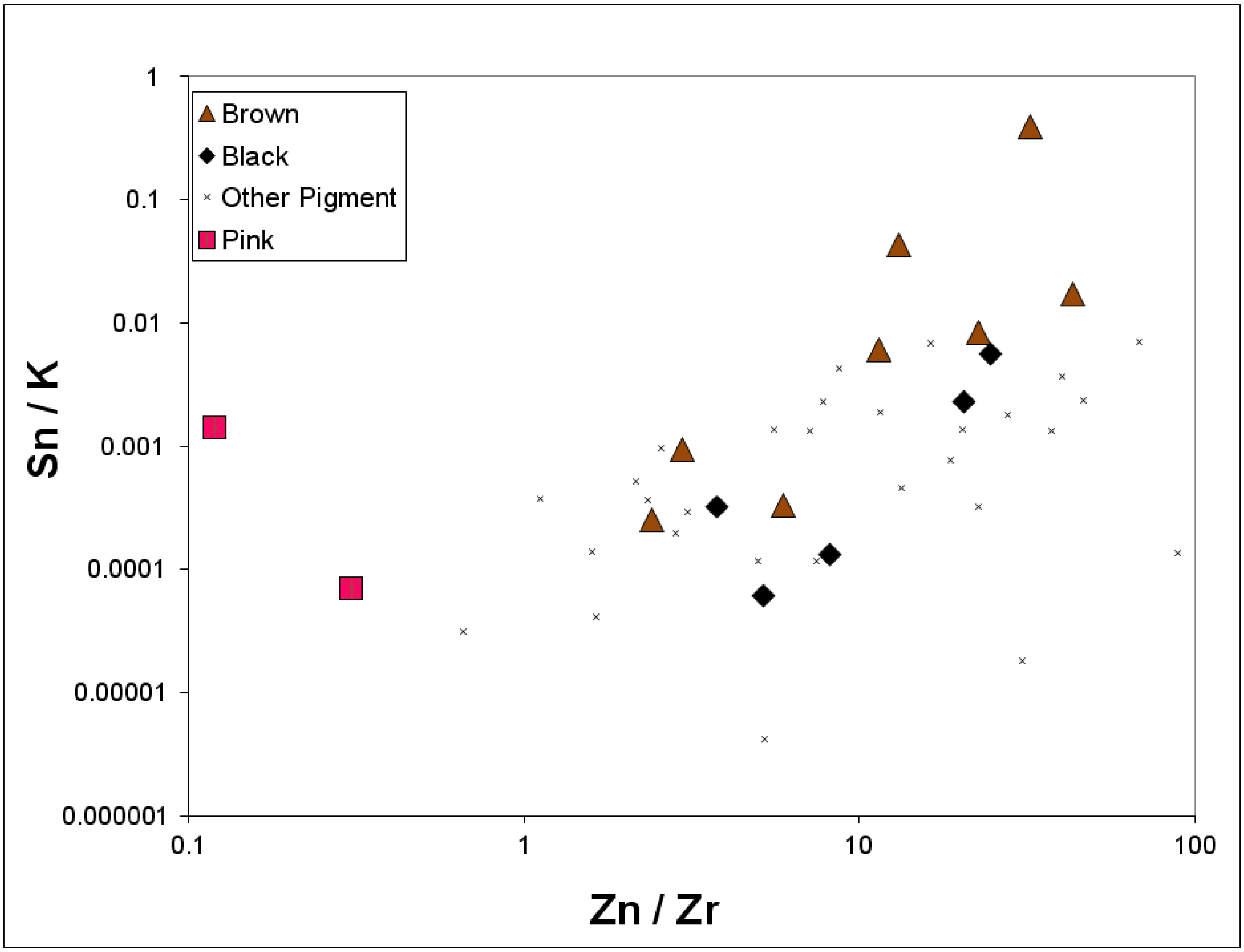


**Figure 9. Relative abundance of Sn and Zr (LA-ICP-MS analysis) highlighting brown and pink pigments.**

upper left of Figure 8 and was mentioned previously as having an organic substrate-like signature. This sample, then, may not actually represent a pigment but instead a substrate. The remaining two wood darts (164A, 484), and both cane darts (751, 754), are depleted in both Fe and Mo, and are unlike the other red pigments. Among the wooden dart samples, 164A was also distinctive for Zn, displaying concentrations nearly 50 times higher than any other pigment, along with elevated levels of Sn, Zr, and Ti. Unfortunately, we were unable to analyze the sample using either XRD or EM.

As in the green pigments, red cane dart pigments stand out as unique from the wooden dart reds. In addition to being low in Fe and Mo, the red pigments on cane darts are chemically unique in terms of other elements or element ratios as well, such as Na (high), Rb/Sr (high), Zn (low), and Al/Ca (low). This suggests that a distinctive mineralogical recipe characterized the reds applied to cane darts and that this recipe was unlike the red pigments applied to the cane arrows later in time. Differences in Rb/Sr ratios may relate to the general geological age of the materials in the pigment, as one isotope of Rb ($^{87}$Rb) decays to $^{87}$Sr over time, but additional isotopic analyses are necessary to verify this.

*Pink*

Two artifacts analyzed by LA-ICP-MS had pigments identified as pink rather than red due to their lighter color; both involved cane darts. One of these was subjected to further EM analysis. For the most part, these pigments are compositionally similar to the red ones, displaying elevated levels of Fe and Zr, and higher levels of Pb and Mo. However, both have much lower levels of Cr and Zn. The pink pigments are shown on the left side of Figure 9, which plots Zn/Zr against Sn/K.

Indeed, one of the pink pigments (480) displayed elevated Rb/Sr, Co and Cu, and extremely elevated levels of Zr, approximately 50–100 times the levels seen in all other pigment samples. Zr was consistently higher in all five ablated spots in this sample, suggesting this result is not the product of the laser hitting a stray zircon grain, but that Zr is found throughout the pigment.

EM-EDS analysis of this sample showed a very fine grained structure, but did not disclose the presence of any zircon or other high-zirconium minerals. Instead, quartz, calcite and a mixture of aluminum-rich silicate minerals were observed. We believe its color is the result of mixing a fine-grained red ochre (hematite) with a light-colored clay mineral rich in Zr. Unfortunately, we were not able to perform XRD on this sample to confirm this mineralogical signature.

*Brown*

Eight pigments were identified as brown in color, ranging from lighter brown to black-brown. These include seven pigments derived from wooden dart shafts and a single pigment on a cane dart. LA-ICP-MS analyses revealed that, relative to other pigments, browns tend to have higher abundances of Sn and Zn (as seen in Fig. 9), and to a lesser degree elevated Ba, Ca, and Sr, and depleted Na. One of the high Sn samples also had highly elevated levels of Zr. However, this was due to one anomalous ablation spot (of five total spots), suggesting the laser may have hit a stray zircon crystal at this location during the analysis. We eliminated this spot from the analysis and averaged the remaining four spots to derive elemental values.

Two brown samples were analyzed by EM, and a third was analyzed by XRD. Of the former, both revealed a thin and fine-grained layer of paint over a wooden substrate. Tin- or zinc-bearing minerals were not evident in either sample. EM-EDS analysis suggested the presence of iron oxides, alkali feldspars, albite, and clay minerals, generally rich in varying mixtures of Fe, Ca, and Mg, in addition to silicon (Si) and Al. We believe the brown colors derive mainly from the addition of a light-colored clay mineral paste to a black base pigmenting agent, perhaps an iron oxide such as limonite with elevated levels of Sn and Zn, and/or a thinner application of a more finely-ground black pigment over a wooden substrate.

*Black*

Five pigments were classified as black and were analyzed by LA-ICP-MS. The samples analyzed included pigments on one wooden arrow, three wooden darts, and one cane dart. The wooden arrow was analyzed by XRD, and one wooden and one cane dart was analyzed by EM.

Compared to other colors, black pigments were the most variable in chemical composition. The wooden arrow (193) was clearly unlike the others, especially in the relative abundance of Mn, which accounted for 22% of the raw element counts and was over 100 times higher than in any other sample. This artifact is highlighted in the lower left side of Figure 8. XRD analyses on this sample revealed (not surprisingly) the presence of manganese oxide, as well as manganese hydroxides and oxyhydroxides. The presence of hydroxides and oxyhydroxides of manganese ores may indicate a natural decomposition of the Mn minerals into other states, or may alternatively indicate that a Mn compound was treated using heat and water, perhaps during preparation of the paint mixture, before its application to the arrow fragment. Mn oxides were not detected in any of the other pigments from Gypsum Cave. Prehistorically, Mn oxides were used in many places around the globe for black colors (e.g., Clottes 1993; Edwards et al. 1999; Striova et al. 2006). Mn oxide is also reported to have been used by various California groups in the Mojave Desert and San Diego areas to the west of Gypsum Cave (Campbell 2007:73).

Black pigments on two of the three remaining items (all wooden darts) are characterized by levels of Cu that are not as high as the malachite-based greens, but are much higher than any other non-green sample. EM-EDS analysis on one of these (147) revealed the presence of a coarse-grained cuprite ($Cu_2O$) and a copper-sulfate ($CuSO_4$; likely chalcanthite, $CuSO_4 \cdot 5H_2O$), confirming the source of the elevated Cu level. These minerals likely contribute to the black color. In addition, quartz, calcite, dolomite, kaolinite ($Al_2Si_2O_5(OH)_4$), and tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) are present as indicated by the EM-EDS analysis of this specimen. The third wooden dart contains high levels of Ca and medium levels of Fe, but is not otherwise especially distinctive in chemical composition. XRD analysis on this latter sample showed the presence of feldspars, as well as gypsum, not only in its natural state, but also as bassanite ($2CaSO_4 \cdot 0.5H_2O$), a mineral that can be formed by heating gypsum (and thereby partially dehydrating it). This may be a charcoal-based pigment mixed with a gypsum-bassanite binder and perhaps an iron-bearing mineral.

Finally, relative to other black pigments, pigment from the cane artifact (754) is especially elevated for Ca and Fe. The EM-BSE image (Fig. 10) revealed a fine-grained paint, while EM-EDS suggested the presence of both alkali and plagioclase feldspars, mixed in a paste of Fe-K-Mg-Al-bearing silicates. Figure 10 highlights a concentration of one of these Fe-rich silicate mixtures. We suggest that these Fe-bearing minerals are producing the black color in this pigment.

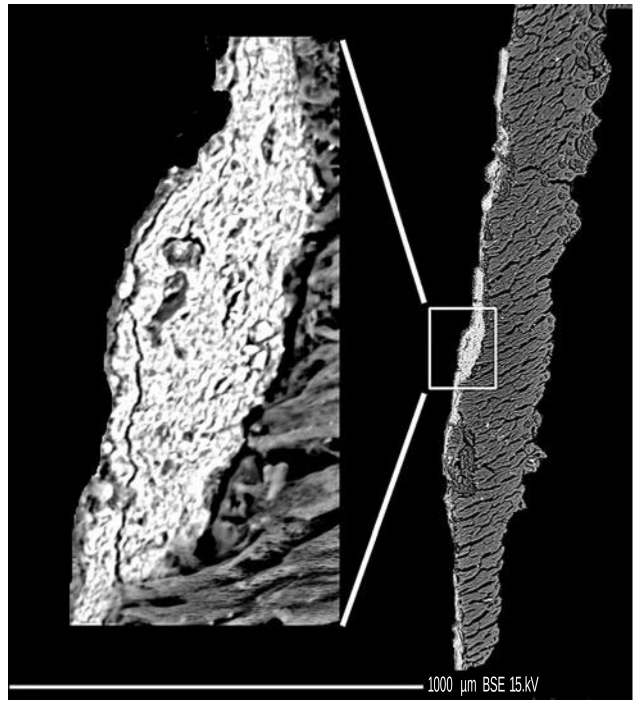


**Figure 10. BSE image of black pigment on artifact 754, with inset highlighting Fe-rich silicate mixture.**

## DISCUSSION

The combined analyses reveal that the pigments from Gypsum Cave were produced from a variety of different minerals. None of the five subjectively-defined colors was characterized by a homogenous/standardized compositional or mineralogical recipe. This indicates that the individuals who used Gypsum Cave exploited a wide range of minerals and blended them in varying amounts to create the palate of colors seen in the weaponry fragments recovered during the archaeological investigations.

The largest pattern in the study is within the green pigments, which strongly divide along a malachite-on-wood and green earth-on-cane line. A similar but weaker pattern exists among the red pigments, where again the reds applied to wooden darts have signatures with elevated Fe and Mo that are distinctive from those placed on cane darts. Although there is only one black applied to a cane dart, it too is different than the black pigments on wooden darts, while brown pigments were not applied to cane darts and pink pigments were applied only to cane darts. Thus, the types of paints applied to wooden darts were different in both mineralogy and chemical composition from those applied to cane darts.

Radiocarbon dating indicates that the wooden and cane darts were in use at the same time. The correlation between substrate type and pigment recipes for the darts raises a number of interesting questions; foremost among them is whether they are part of a single assemblage used by one cultural group, or if they effectively represent two separate assemblages, possibly the result of different groups from different regions making use of the cave.

As at Gypsum Cave, a number of other caves in the region dating to the same time period contain comingled wooden and cane dart fragments, including Pintwater Cave (Buck and DuBarton 1994), Black Dog Cave (Winslow and Blair 2003), Firebrand Cave (Blair and Winslow 2006), and Newberry Cave (Davis and Smith 1981). This suggests that cane and wood were commonly used concurrently. Furthermore, various pieces of cane and wood recovered from Gypsum Cave suggest that these pieces may have been used as part of the same composite tool. At minimum, a dart consists of a mainshaft (of either wood or cane) with one cupped end that fits on an atlatl spur, and a stone-tipped foreshaft that fits on the opposite end of the mainshaft, comprising a two-piece dart. However, pieces from Gypsum Cave show that darts with three or more parts, including one or more midshaft tube couplers, were also commonly used. Such couplers come with female-female, female-male, and male-male ends, and were made from both cane and wood. These sections were used in combination to build a complete dart of the desired length, much as a pipefitter builds a line to the desired shape and length from various fittings. This suggests that cane and wood went together and that the assemblage from Gypsum Cave was used by one cultural group. Furthermore, combining wood and cane into a single weapons system was a region-wide phenomenon.

Yet we are still left to wonder about the behavioral significance behind using one suite of pigment recipes for cane and another suite for wooden weaponry. Several possible explanations come to mind. Perhaps the group using Gypsum Cave had a residential mobility pattern that gave them access to diverse material in the course of their rounds. Thus, cane *Phragmites* and the pigment materials applied to it may have come from one region, while the arrowweed used for the wooden weaponry (Wigand 2009) and the pigment materials applied to it came from another. This might be tested by using Sr-isotope analysis on the substrate, for example, to see if the cane and wood grew in different regions (e.g., English et al. 2001, Reynolds et al. 2005). However, the finding that the reds on arrows are most similar to many of the reds on darts does not fit comfortably with this explanation. Alternatively, perhaps the group using the cave earlier in time obtained part of their dart weaponry assemblage through trade, acquiring painted cane segments that were fabricated in a different region, for example.

On the other hand, practical, or even religious and/or traditional beliefs, might be at the root of some of this behavior. Practically speaking, perhaps malachite did not adhere well to the smooth, waxy surface of cane, and in order to achieve the desired color effect, different recipes using green earth were followed, depending upon whether they were to be applied to cane or to wood. While this may explain patterns in the greens, it does not explain patterns in the reds. Again, recipes for the reds for cane and wooden darts are dissimilar, but cane arrows group with many of the wooden darts.

Concerning religious and/or traditional beliefs, it is a fact that—throughout the world—many cultures attach particular significant to different colors. Contemporary Native American groups in the Great Basin, American Southwest, and along the Colorado River impart symbolic importance to specific colors. The complexity of color symbolism among the Hopi is particularly well developed and has been widely reported, with red, for example, being associated with a particular direction, a particular tree used for building material, particular places in the traditional landscape, a particular bird used in ritual, a particular flower associated with girls, and so forth (Hieb 1979). For the Chemehuevi, Laird (1976:101) reported that different colors of corn were associated with different clans of the dead. Furst (2008:52–55) has reviewed appropriate uses and restrictions concerning different paint colors among the Mojave people, even noting that the "Mojaves lacked a source of red pigment and bartered for it with their Walapai neighbors, who found it at Red Mountain in their own lands," while black paint, "perhaps manganese rock" may have been directly obtained by them from a "place south of Topok they called Black Mountain" (2008:54, citing Devereaux 1949:111). In addition, Applegate (1979) has discussed the significance of colors for the Luiseño, where certain colors were considered dual opposites (e.g., red and black) and were associated with sex, cardinal directions, and other concepts. Technological experiments and additional analyses on pigments from other nearby caves would help to address some of these possibilities.

We also noted that some pigments were particularly coarse in texture. For example, all the malachite-based pigments contained large aggregate clasts of malachite. Campbell (2007:77) reports that some minerals are more vibrant in color when left in a coarse state. In particular, malachite becomes less saturated in color with decreasing average particle size. This may explain why malachite-based greens only appear on wooden implements. If coarse-grained pigment pastes do not adhere well to cane surfaces, malachite may not have been an option for getting green pigments on such a medium, and green earths may have been a substitute.

Within particular colors, especially within the reds, there was evidence of significant and patterned variation in the geochemistry of the pigments. Thus, there appear to be at least two different red "recipes," varying especially in their iron and manganese content. Likewise, several brown pigments had elevated levels of Sn, one pink pigment displayed notably high Zr, one black was based on manganese oxide and another on cuprite, and one red appears to contain a zinc-based compound. Why such variation exists within the sample of pigments is not known, but may indicate different pigmenting traditions, different raw material availability for artisans, experimentation with different minerals, or attempts to produce different shades or lusters of particular colors. Additional research, especially utilizing a larger sample size, will be necessary to begin addressing these issues.

At the same time, while there was significant mineralogical and geochemical variation within particular colors, there were no systematic differences detected by weapon type (e.g., dart vs. arrow). This suggests there was some degree of continuity in pigment recipes over time, though our sample of arrows is small (n = 4).

## CONCLUSIONS

This paper presents a first step towards understanding pigment use in the southwestern Great Basin by describing, geochemically and physically, the composition of prehistoric pigments. The analyses confirmed notions proposed in previous studies of pigments (e.g., Campbell 2007; Scott et al. 2002), such as the suggestion that malachite and green earths (e.g., glauconite, celadonite) were used to produce greens, and hematite was used to produce reds.

Documenting pigment composition is important, but ultimately we are interested in how these pigments can inform us anthropologically about ancient human behavior in the region. In this regard, the study demonstrated that interesting patterning existed within colors and between color and substrate type, but produced more questions than it answered. For example, analyses revealed the presence of many other non-pigmenting minerals within the paint, such as quartz, feldspar, gypsum, and various alumina-silicate minerals. It is unclear whether these were contaminants from sediments within the cave or were intentionally added to the pigments. EM data suggest that many of these minerals are deeply embedded within the pigment matrix, and do not occur just on surfaces as would be expected of a contaminant. This suggests an intentional addition, perhaps as an extender or binder of some sort, but additional analyses are necessary.

In the future, we hope to undertake similar studies with other weaponry in the southwestern Great Basin. For example, weapons with pigments have been reported in Firebrand Cave (Blair and Winslow 2006) less than 30 km. to the east of Gypsum Cave, and from Newberry Cave (Davis and Smith 1981) in the Mojave Desert of California. Such studies would place the Gypsum Cave pigments in a better geographic and cultural context, and provide greater behavioral meaning for pigment production and use in the desert west of North America. As well, we hope to (or hope others will) undertake parallel studies documenting the nature and location of potential sources for the different minerals used by ancient artisans; such data would be especially informative about issues concerning ancient mobility practices.

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