Title

X-RAY FLUORESCENCE (XRF) ANALYSIS OF MAJOR, MINOR, AND TRACE ELEMENTS OF NATIVE COPPER NODULES AND COPPER BELLS FROM SOUTH DIAMOND CREEK (LA 181765) AND TWIN PINES PUEBLOS (LA 75947), SOUTHERNNEW MEXICO

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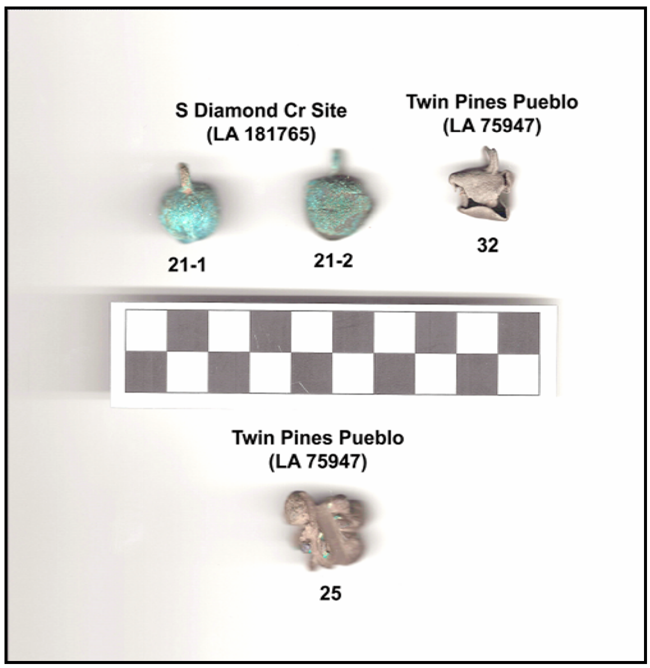

Sample of copper bells (top) and "fetish" (lower) from the South Diamond Cr site and Twin Pines Pueblo

by

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INTRODUCTION

The analysis here of 10 native copper nodules (Figure 1), 13 copper bells, and one copper fetish (see cover image), suggests the possibility of local production of the fetish, and possibly the bells (see Table 1 and Figures 2 and 3). However, the proportion of Cu in the bells is over 91%, many near 99% and the proportion of corresponding trace elements so low that based on XRF, and the lack of data from known copper artifact production centers (i.e. Paquimé, northern Chihuahua) no confident assignments can be made at this time. The elemental and statistical correspondence between the copper nodules and the bells is generally very high, however. Analysis of local copper ore and elemental data from other copper artifacts and copper sources could shed light on the issue.

LABORATORY SAMPLING, ANALYSIS AND INSTRUMENTATION

Given the nature of prehistoric copper production, two methods/calibrations were used for x-ray fluorescence analysis. Major and minor oxides and trace elements were acquired with a method specific for metals in tandem with the trace element analysis used for rocks (http://swxrflab.net/anlysis.htm).

All the samples are analyzed whole. The results presented here are quantitative in that they are derived from "filtered" intensity values ratioed to the appropriate x-ray continuum regions through a least squares fitting formula rather than plotting the proportions of the net intensities in a ternary system (McCarthy and Schamber 1981; Schamber 1977). Or more essentially, these data through the analysis of international rock standards, allow for inter-instrument comparison with a predictable degree of certainty (Hampel 1984; Shackley 2011).

All analyses for this study were conducted on a ThermoScientific *Quant'X* EDXRF spectrometer, located at the Geoarchaeological XRF Laboratory, Albuquerque, New Mexico. It is equipped with a thermoelectrically Peltier cooled solid-state Si(Li) X-ray detector, with a 50 kV, 50 W, ultra-high-flux end window bremsstrahlung Rh target X-ray tube and a 76 µm (3 mil) beryllium (Be) window (air cooled), that runs on a power supply operating 4-50 kV/0.02-1.0 mA at 0.02 increments. The spectrometer is equipped with a 200 l min^{-1} Edwards vacuum pump, allowing for the analysis of lower-atomic-weight elements between sodium (Na) and scandium (Sc). Data acquisition is accomplished with a pulse processor and an analogue-to-digital converter. Elemental composition is identified with digital filter background removal, least squares empirical peak deconvolution, gross peak intensities and net peak intensities above background.

The analysis for mid Zb condition elements Ti-Nb, Pb, Th, the x-ray tube is operated at 30 kV, using a 0.05 mm (medium) Pd primary beam filter in an air path at 100 seconds livetime generally using an 8.8 mm tube collimator to generate x-ray intensity Ka-line data for elements titanium (Ti), manganese (Mn), iron (as $Fe_2O_3^T$), cobalt (Co), nickel (Ni), copper, (Cu), zinc, (Zn), gallium (Ga), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), niobium (Nb), lead (Pb), and thorium (Th). Not all these elements are reported since their values in many volcanic rocks are very low and below detection limits. Trace element intensities were converted to concentration estimates by employing a linear calibration line ratioed to the Compton scatter established for each element from the analysis of international rock standards certified by the National Institute of Standards and Technology (NIST), the US. Geological Survey (USGS), Canadian Centre for Mineral and Energy Technology, and the Centre de Recherches Pétrographiques et Géochimiques in France (Govindaraju 1994). Line fitting is linear (XML) for all elements. When barium (Ba) is analyzed in the High Zb condition, the Rh tube is operated at 50 kV and up to 1.0 mA, ratioed to the bremsstrahlung region (see Davis 2011; Shackley 2011). Further details concerning the petrological choice of these elements in Southwest volcanic rocks is available in Shackley (1995, 2005; also Mahood and Stimac 1990; and Hughes and Smith 1993). Nineteen specific pressed powder standards are used for the best fit regression calibration for elements Ti-Nb, Pb, Th, and Ba, include G-2 (basalt), AGV-2 (andesite), GSP-2 (granodiorite), SY-2 (syenite), BHVO-2 (hawaiite), STM-1 (syenite), QLO-1 (quartz latite), RGM-1 (obsidian), W-2 (diabase), BIR-1 (basalt), SDC-1 (mica schist), TLM-1 (tonalite), SCO-1 (shale), NOD-A-1 and NOD-P-1 (oceanic manganese) all US Geological Survey standards, NIST-278 (obsidian), U.S. National Institute of Standards and Technology, BE-N (basalt) from the Centre de Recherches Pétrographiques et Géochimiques in France, and JR-1 and JR-2 (obsidian) from the Geological Survey of Japan (Govindaraju 1994).

Metal Oxide Analysis

Analysis of the major metal specific oxides of Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Sn, Sb, Au, and Pb is performed under the multiple conditions elucidated below. This fundamental parameter analysis (theoretical with standards), while not as accurate as destructive analyses (pressed powder and fusion disks) is usually within a few percent of actual, based on the analysis of US Mint 2007 US Dollar standard (see also Shackley 2011). The fundamental parameters (theoretical) method is run under conditions commensurate with the elements of interest and calibrated with four metal standards: Mo pure, Pb pure, Cu pure, and US Mint 2007 US Dollar.

Conditions Of Fundamental Parameter Analysis[1]:

Mid Zb (Ag, Mo, Sn, Sb)

Voltage	30 kV	Current	Auto
Livetime	60 seconds	Counts Limit	0
Filter	Pd (0.06 mm)	Atmosphere	Vacuum
Maximum Energy	40 keV	Count Rate	Medium

High Zb (Mn, Fe, Co, Ni, Cu, Zn, Au, Pb)

Voltage	50 kV	Current	Auto
Livetime	60 seconds	Counts Limit	0
Filter	Cu (0.559 mm)	Atmosphere	Vacuum
Maximum Energy	40 keV	Count Rate	High

[1] Multiple conditions designed to ameliorate peak overlap identified with digital filter background removal, least squares empirical peak deconvolution, gross peak intensities and net peak intensities above background.

[2] Current is set automatically based on the mass absorption coefficient.

The data from the WinTrace software were translated directly into Excel for Windows software for manipulation and on into JMP 12.0.1 for Windows for statistical analyses. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. For trace elements, RGM-1 a USGS rhyolite standard was analyzed during each sample run to check machine calibration since it has been used in North American XRF analyses for decades (Shackley 2011; Table 1 here). For metal oxide analysis, a US Mint 2007 US Dollar standard was used.

Trace element data exhibited in Table 1 is reported in parts per million (ppm), a quantitative measure by weight, and percent by weight as noted.

DISCUSSION

X-ray fluorescence spectrometry (XRF) has been used for the analysis of copper objects since XRF moved into the realm of archaeological endeavor (Cockrell et al. 2015; Hall 1960; Olsen 1963; Shackley 2011). Recently, both portable XRF (pXRF) and laboratory XRF have been used in the analysis of copper objects, including gold and copper bells in Mesoamerica with some success (see Cockrell et al. 2015). However, there are two issues that arise in the XRF analysis for provenance of both source and artifact composition. The first, and an issue in all provenance studies, is the quality of source data, in this case copper sources (Figure 1). Secondly, most prehistoric North American copper bells are produced from smelted copper during a lost-wax method, and given that smelting even in Mesoamerica is not an exacting process, the composition can vary greatly (Cockrell 2014; Haury 1947; Hawley 1953; Olsen 1962; Palmer et al. 1998; Ross 1968; Simmons et al. 2009). Frustrating the first issue is that it is impossible to determine whether all copper sources are known in the greater North American Southwest, and more importantly native copper is near 100% copper in composition with few or no accessory minerals or elements (Blakemore et al. 2016; Boyce 2015; Cockrell et al. 2015; Palmer et al. 1998; Ross 1968; see Table 1 and Figure 2 and 3 here). The copper bells at Chaco are native copper with an analyzed copper composition of 100% with no other detectable elements at least with the PIXE analysis of Palmer et al. (1998) as reported.

The first stage of the analysis was focused on the assemblage proper, the Twin Pines and South Diamond Creek sites, in order to investigate the variability within the copper artifacts, and determine the compositional relationship between the native copper nodules and the artifacts, if any. The next step was to compare this data set to some of the few Southwestern copper artifacts that have been analyzed in such a manner to be compatible with the XRF results here.

The Twin Pine and South Diamond Creek Copper Objects

The first step was to plot the elemental values that seemed to be most operating in the data with 95% confidence ellipses as an overlay in the plots. Obviously Cu, but the accessory elements Mn, Fe, Ag, and Pb exhibited the higher values, although some were below the detection limits (see Table 1 and Figure 2). The primary question is whether there is a compositional relationship between the artifacts (bells, clappers, and fetish), and the native copper nodules (the one "pendant" was a modern brass with relatively high Zn). Immediately apparent is that while there is a strong overlap between the native copper nodules and the artifacts, the relationship was not 100% (see Figures 3 and 4). The best fit between the native copper and the artifacts is with Mn, and Fe, two elements commonly found in copper ore (Figure 3). Consistently, however a few of the bells were outside the 95% ellipses that included the native copper. If these bells are smelted, then this would be a consequence even if the bells were produced from the same copper as the nodules. One way to ascertain the level of variability in the elements of interest is to subject them to a principal components analysis by artifact type (Figure 4). In those objects with component variability greater than 1 or -1, these objects can be seen as outside the main group. As can be seen in the plot of the first two components that include 93.5% of the variability using the elements Mn, Fe, Cu, and Pb, there is a good statistical relationship between most of the artifacts and the native copper with some variability (Figures 3 and 4). The clapper (sample 27) and bell (sample 24) from Twin Pines, and the bell (sample 43) from South Diamond Creek Pueblo are most divergent on these components. It is not clear what the variability means metallurgically. During the smelting process, if indeed these are smelted, some contamination is possible. What could shed some light on this variability is a comparison with copper artifacts from other archaeological contexts in the Southwest (see below).

Paquimé (Casas Grandes) and the Mimbres Sites

The most complete compositional data set for copper bells in the Southwest is the Palmer et al. (1998) particle induced x-ray emission spectrometry microprobe (PIXE) study including bells from Paquimé (Casas Grandes) in northern Chihuahua approximately 250 km south of the project sites. In the Palmer et al. (1998) study the bells were typologically analyzed from Chaco, as well as all the other sites using DiPeso et al. 1974 typology, but all of the bells analyzed from Chaco contained only pure copper with no accessory minerals or elements detected, and so are compositionally different from other Southwestern bells (cf. Shackley 2017; Palmer et al. 1998). It appears that the results from PIXE and XRF are statistically compatible in nearly all elements, NAA less so for reasons discussed elsewhere (Glascock 2011; Poupeau et al. 2010). Therefore, the data from the analysis of Paquimé and other Southwestern copper artifacts discussed here should be compatible with this analysis. Indeed that seems to be the case (see Palmer et al. 1998). Having said that, it is important to note that the PIXE analyses while instrumentally compatible are not as accurate as more recent XRF instrumentation for many elements (Poupeau et al. 2010; Shackley 2011). PIXE microprobes focus on a very small area and so multiple analyses must be taken and, given the heterogeneity inherent in copper ore, sometimes the variability between areas sampled could be great (see Palmer et al. 1998, Table 2 here). X-ray fluorescence spectrometry focuses on a much larger area, essentially producing a mass analysis of the composition and thus "averaging" the composition of that area irradiated (Shackley 2011). Palmer et al's. (1998) multiple PIXE analyses of the copper bells were summed and the mean calculated for this comparison thus averaging the multiple analytical spots (see Table 2).

There is no direct evidence of prehistoric smelting in the Southwest outside the possibility at Paquimé (Boyce 2015; Palmer et al. 1998; Ross 1968). Copper sources are, of course, common throughout the Southwest, including the region in and around southern New Mexico and northern Chihuahua (see Figure 2). Unfortunately, there has been no analyses of the composition of copper sources in the Southwest specifically for archaeological purposes and especially XRF elemental data, but as mentioned above free copper is essentially 100% copper with few accessory minerals or elements that could make discrimination possible. Given the lack of smelting technology in the prehistoric Southwest north of Chihuahua, and issues in the analysis of the composition, this study is restricted to the available data from the Palmer et al. (1998) study.

Copper bells have been recovered from a number of archaeological contexts in the North American Southwest, including Paquimé and Chaco, as well as Snaketown and other preclassic Hohokam sites (see Figure 2). However, few of these bells have been analyzed in such a way that they can be compared successfully to XRF results (c.f. Palmer et al. 1998). The bells from Pueblo Bonito and Pueblo del Arroyo at Chaco were produced from pure copper with no other elements detected, unlike the other copper artifacts here and in the Palmer et al (1998) study. The Paquimé bells were analyzed by PIXE and are more relevant for comparison. However, comparison with the NAA analyzed data for the sites other than Paquimé in Palmer et al. (1998) was attempted with Cu, Rb, Sr, Ag, and Pb elements with some success (Table 2). Re-analyzing the Paquimé, and Chaco bells with XRF would be a logical first step in unraveling the inter-laboratory analytical issues (see Summary comments below).

Analysis and Results

Both a multivariate statistical analysis using bivariate scatterplots with 95% confidence interval ellipses and principal component multivariate analysis using the elements Cu, Rb, Sr, Ag, and Pb as variables was used to discriminate the copper objects as in the site level analyses (Figures 4 and 5). Additionally, using multivariate principal component analysis "against" a bivariate plots of the same elements is a good check on the validity of multivariate groupings and vice-versa (Baxter 1992; see also Glascock 2011).

Using elements Cu, Rb, Sr, Ag, and Pb, often at a level above the detection limits of PIXE and XRF, the multivariate analysis and plots with confidence ellipses are in good agreement (Figures 1 and 3). Note that as with the artifacts in the two sites, the copper bell from LA 117502 on White Sands does not plot anywhere near other bells and copper nuggets from the Southwest. Using these elements and the Palmer et al. (1998) data this bell appears to have been produced from a very different composition, as in the case of the two bells and clapper in the Mimbres sites, as well as on bell from Paquimé and two bells (31 and 32) from South Diamond Creek Kiva (Tables 1 and 2; Figures 4 and 5). What is more interesting, also evident from the White Sands study, is that many of the bells are produced from the same composition all over the Southwest including some from Paquimé, and including many of the copper objects from the two project sites (Figures 2 and 3). This brings up an important point. At this time it is impossible to know if this is due to the variability introduced during smelting, different copper sources, or the variability between the two instrumental methods as discussed above (see Cockrell et al. 2015). The best way to determine this is by analyzing all these artifacts by one method.

Cockrell (2014), Cockrell et al (2015) and Simmons et al. (2009) in Maya contexts in Mesoamerica note the probability that these bells were curated across generations, and could be kept in a family for decades if not hundreds of years. This could have ramifications for the deposition and chronology in the Southwest, as well. According to Boyce (2015:37) there are two periods where bells were recovered from Southwestern contexts: Period I dating from AD 650-1200 where only pure copper bells with trace elements were produced; and Period II from AD 1100/1200-1521, where both pure copper and smelted bells were produced. It is unclear how the composition was determined, since many of the hundreds of copper bells recovered from the Southwest have never been compositionally analyzed. Be that as it may, the bells from these Mimbres sites would be considered pure copper bells with trace elements.

SUMMARY

It does appear that the majority of copper objects recovered from these two project sites, both native nodules and artifacts could have been produced from the same production event or possibly the same smelter, and that the composition is similar to some other copper bells throughout the Southwest, including Paquimé. Some of the artifacts, however, at least as evident in this data set, do not match any others from the Southwest. A final point is that there are a number of issues that could serve to represent the variability seen here, mainly comparing the results of two instrumental analyses could be the major factor in that variability. Where copper production events occurred whether it was at Paquimé or points north remains a mystery.

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Table 1. Elemental concentrations for the native copper nodules and copper artifacts, 2007 US Mint Dollar standard, and USGS RGM-1 rhyolite standard. Measurements in wt. percent (%) or parts per million (ppm) as noted. Elements with brackets above 0 are below the detection limits at 1 SD.

SAMPLE	SITE	Mn	Fe	Co	Ni	Cu	Zn	Mo	Ag	Sn	Sb	Au	Pb	Artifact Type
		%	%	%	%	%	%	%	%	%	%	%	%	
3	Twin Pines	[0.002]	0.717	0.014	0.025	99.111	0.013	0.046	0.016	0.004	0.052	0	[0.001]	native copper
22	Twin Pines	0.011	2.771	0.005	0.021	96.971	0.006	0.113	0.032	0	0.011	0.008	0.051	native copper
23	Twin Pines	0.024	3.808	0.015	0	95.234	0.018	0.023	0.766	0	0.062	0.02	0.031	bell
24	Twin Pines	0.034	4.376	0	0.026	93.359	0.013	0.061	1.176	0.034	0.748	0.005	0.169	bell
25	Twin Pines	0.036	4.204	0.007	0.018	95.576	0	0.026	[0.021]	0.037	0.009	0	0.066	fetish
26	Twin Pines	0.022	1.491	0	0.014	98.242	0.006	0	[0.01]	0.044	0.139	0.018	[0.013]	native copper
27	Twin Pines	[0.002]	0.79	0.01	0.015	98.355	0.064	0	0.504	0	0.042	0.019	0.199	clapper
28	Twin Pines	0.045	4.446	0	0.013	94.296	0.073	0	0.503	0.05	0.483	0	0.091	clapper
29	Twin Pines	0.024	2.669	0.01	0.001	97.232	0	0.035	[0.012]	0.009	-0.007	0	[0.015]	native copper
30	Twin Pines	0.017	1.004	0.014	0.005	98.926	0	0.046	[0.005]	0	-0.025	0.001	[0.007]	native copper
31	Twin Pines	0.018	1.353	0.005	0.005	97.414	0.019	0	0.949	0.004	0.12	0	0.112	bell
34	Twin Pines	[0.007]	0.858	0	0.01	99.101	0	0.008	[0.005]	0.01	-0.024	0.005	0.021	native copper
42	Twin Pines	0.044	5.696	0	0.009	93.802	0	0.279	0.103	0.022	-0.007	0	0.053	native copper
50	Twin Pines	0.036	2.835	0.009	0.015	95.672	0.012	0	1.309	0	0.023	0	0.089	bell
52	Twin Pines	0.029	2.314	0.005	0.003	97.498	0	0.059	[0.013]	0	0	0	0.08	native copper
55	Twin Pines	0.015	2.108	0.003	0.005	96.886	0.015	0.017	0.836	0	0.074	0	0.042	bell
101	Twin Pines	[0.005]	1.616	0.01	0.017	87.927	9.495	0	0.618	0.131	0.042	0.059	0.081	brass pendant
102	Twin Pines	0.037	4.665	0.017	0.006	95.174	0	0	0	0.005	0.058	0	0.038	native copper
10	S Diamond Cr Pueblo	0	0.43	0.008	0.003	96.837	0	1.96	0.705	0.026	0.028	0	[0.003]	native copper
21-1	S Diamond Cr Pueblo	[0.001]	0.743	0.007	0.013	98.697	0	0	0.446	0	0.064	0	0.029	bell
21-2	S Diamond Cr Pueblo	[0.004]	0.651	0.004	0.022	98.787	0.002	[0.021]	0.336	0	0.096	0.009	0.068	bell
43	S Diamond Cr Pueblo	0.027	4.551	0.006	0.008	94.488	0.009	0	0.521	0	0.221	0	0.169	bell
32	S Diamond Cr Kiva	[0.004]	2.181	0.003	0.02	96.94	0.009	0	0.518	0	0.242	0	0.084	bell
49	S Diamond Cr Kiva	0.048	2.652	0.025	0.018	96.587	0.008	0	0.562	0	0.052	0	0.049	bell
88	S Diamond Cr Kiva	0.050	7.07	0.002	0.022	91.131	0	0	1.469	0	0.101	0	0.156	bell
89	S Diamond Cr Kiva	0.040	6.444	0	0.018	92.295	0	0	0.888	0	0.245	0	0.07	bell
2007USDOLLAR		3.841	0.295	0.027	4.593	84.12	7.058	0	0.009	0.01	0.021	0.017	0.009	
SAMPLE	**SITE**	**Ti**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Ba**	**Th**					
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm					
3	Twin Pines	5245	12	25	4	19	40	18	107					
22	Twin Pines	14920	58	50	45	70	64	29	63					

23	Twin Pines	8514	27	52	16	57	41	0	75					
24	Twin Pines	14870	88	90	17	114	42	0	46					
25	Twin Pines	18169	105	145	20	150	47	3868	58					
SAMPLE	**SITE**	**Ti**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Ba**	**Th**					
26	Twin Pines	5277	42	137	6	23	31	41	54					
27	Twin Pines	3148	15	14	4	16	33	13	16					
28	Twin Pines	7468	46	90	15	159	35	92	41					
29	Twin Pines	17792	97	178	30	98	33	129	87					
30	Twin Pines	10656	67	147	6	50	58	492	43					
31	Twin Pines	10248	40	62	4	16	74	0	62					
34	Twin Pines	5922	53	110	4	32	95	182	84					
42	Twin Pines	16961	155	181	41	306	57	680	63					
50	Twin Pines	9074	47	110	4	82	29	88	39					
52	Twin Pines	21513	59	105	11	157	59	76	88					
55	Twin Pines	14070	74	133	6	47	83	0	105					
101	Twin Pines	13708	30	63	41	42	190	71	87					
102	Twin Pines	13935	117	118	37	205	53	438	38					
10	S Diamond Cr Pueblo	3578	13	123	23	16	65	453	67					
21-1	S Diamond Cr Pueblo	8450	34	275	44	26	82	280	86					
21-2	S Diamond Cr Pueblo	6045	0	190	20	16	81	158	63					
43	S Diamond Cr Pueblo	16020	95	73	32	109	35	140	37					
32	S Diamond Cr Kiva	11667	78	120	40	31	76	72	58					
49	S Diamond Cr Kiva	10298	66	159	30	86	56	88	49					
88	S Diamond Cr Kiva	12415	151	223	35	175	32	207	33					
89	S Diamond Cr Kiva	10265	121	160	32	147	48	93	35					
RGM1-S4		1593	151	108	29	222	5	811	19					

Table 2. Selected copper wt. percent, and trace elements for the project sites, and copper artifacts from various Southwestern sites. Bracketed elements are below detection limits from this lab's data, and not included in statistical analyses.

SAMPLE	SITE	Type	Cu (%)	Rb (ppm)	Sr (ppm)	Ag (ppm)	Pb (ppm)
10	LA 32079	nodule	99.156	0	87	[83.6]	106
12	LA 32079	nodule	98.852	13	420	[85.8]	66
13	LA 32079	bead	96.003	24	866	12016	73
15	LA 32079	bead	98.526	43	278	3993	35
13-1	LA 117502	nodule	99.574	26	9	0	21
15-1	LA 117502	bead	97.180	16	179	6970	88
18	LA 117502	bell	89.842	15	30	14664	462
22	Twin Pines	nodule	96.970	58	50	[320]	70
23	Twin Pines	bell	95.230	27	52	7660	310
24	Twin Pines	bell	93.360	88	90	11760	1690
25	Twin Pines	bell	95.580	105	145	[210]	660
27	Twin Pines	clapper	98.360	[15]	[14]	5040	1990
28	Twin Pines	clapper	94.300	46	90	5000	910
29	Twin Pines	nodule	97.230	97	178	[120]	42
30	Twin Pines	nodule	98.930	67	147	[50]	59
31	Twin Pines	bell	99.100	40	62	9490	1120
34	Twin Pines	nodule	99.100	53	110	[50]	211
42	Twin Pines	nodule	93.800	155	181	1030	50
50	Twin Pines	bell	95.670	47	110	13090	890
52	Twin Pines	nodule	97.500	59	105	[130]	164
55	Twin Pines	bell	96.890	74	133	8360	420
102	Twin Pines	nodule	95.170	117	118	0	34
43	S Diamond Creek	bell	94.490	95	73	5210	229
21-1	S Diamond Creek	bell	98.700	34	275	4460	101
21-2	S Diamond Creek	bell	98.790	0	[20]	3360	680
32	S Diamond Creek Kiva	bell	96.940	78	120	5180	188
49	S Diamond Creek Kiva	bell	96.590	66	159	5620	61
88	S Diamond Creek Kiva	bell	91.130	151	223	14690	130
89	S Diamond Creek Kiva	bell	92.290	121	160	8880	53
1	Paquimé	bell	93.306	17	8	2920	112
2	Paquimé	bell	99.234	13	7	3100	110
3	Paquimé	bell	99.408	19	50	1268	2530
4	Paquimé	bell	99.900	10	6	295	30
5	Paquimé	bell	99.900	10	8	299	35
6	Paquimé	bell	99.900	12	8	882	36
7	Paquimé	bell	99.815	15	9	1163	48

SAMPLE	SITE	Type	Cu (%)	Rb (ppm)	Sr (ppm)	Ag (ppm)	Pb (ppm)
8a	Paquimé	bell	99.824	9	5	577	114
8b	Paquimé	bell	99.827	12	7	1148	30
9	Paquimé	bell	99.813	11	7	1086	67
10	Paquimé	bell	99.857	11	7	1226	53
11	Paquimé	bell	99.600	7	4	20	508
12	UT/AZ	bell	n/a	8	5	1209	60
13	AZ BB:6:2	bell	n/a	n/a	26	1161	252
14	Gatlin Site, AZ	bell	n/a	n/a	23	689	140
15	LA 416, Pottery Mound	bell	n/a	n/a	45	209	117
16	UT	bell	n/a	n/a	2298	73	205
17	Copper Bell Ruin, AZ	bell	n/a	n/a	35	791	245
18	Pollack Site, NA 4317, AZ	bell	n/a	n/a	39	53	150
19	Sundown, NA 16385, AZ	bell	n/a	n/a	48	79	213
20	Sundown, NA 16385, AZ	bell	n/a	n/a	30	36	153

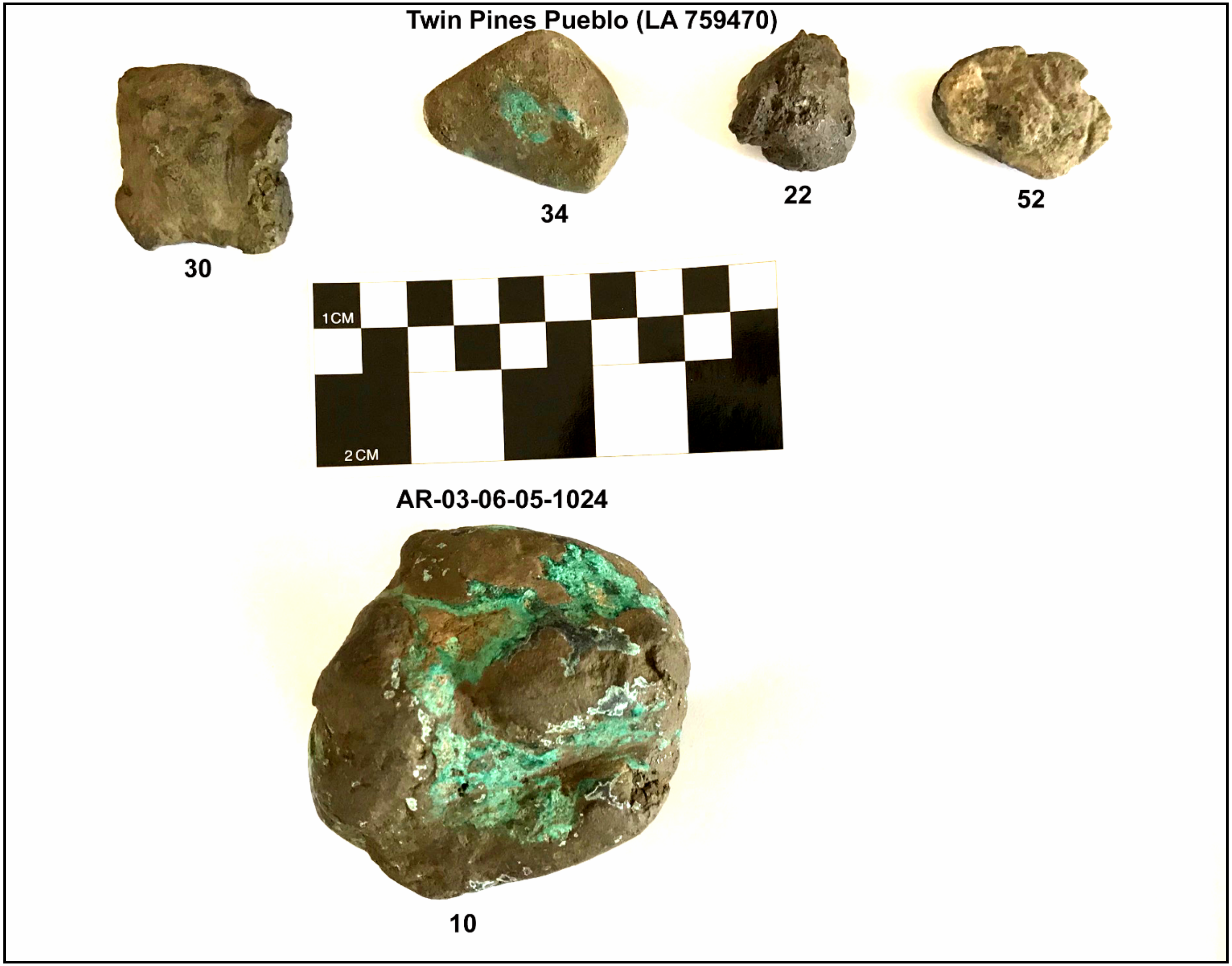

Figure 1. Selected copper nodules from project sites (see composition in Table 1). Green on the surfaces is likely malachite [$Cu_2CO_3(OH)_2$] frequently associated with copper ores.

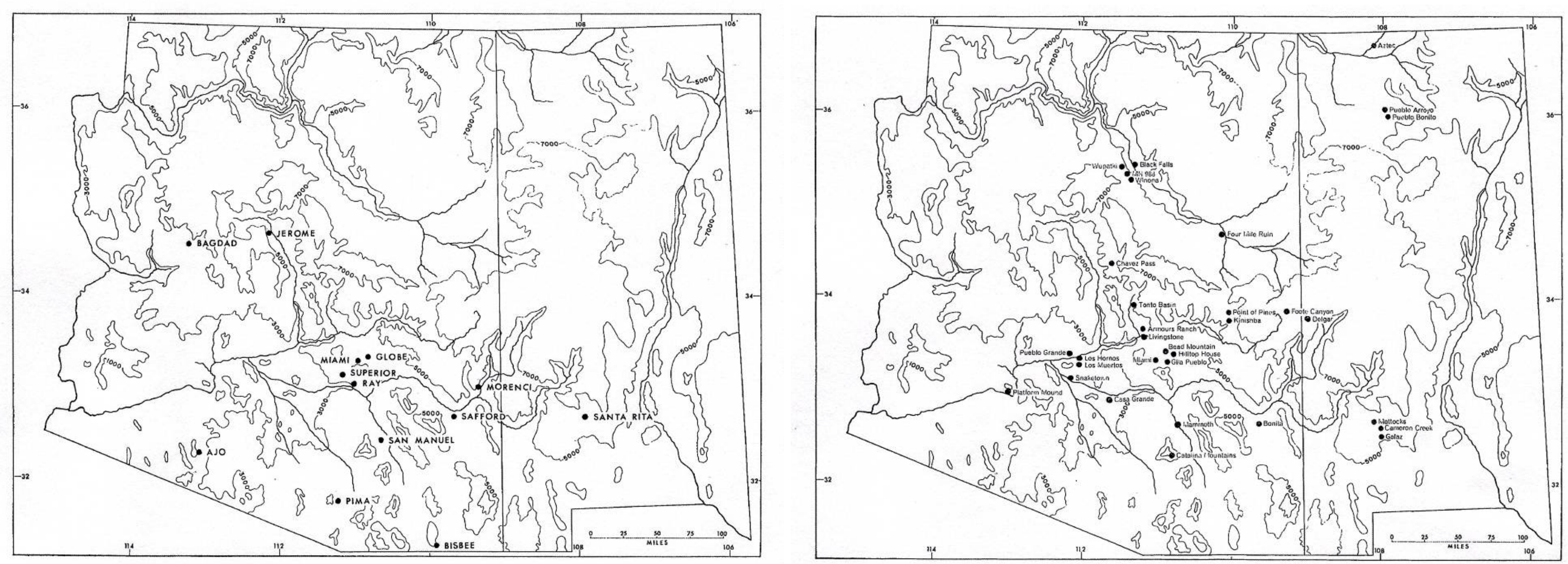

Figure 2. Known sources of copper in the American Southwest as of 1968 (left), and archaeological sites where copper bells had been recovered (right). Adapted from Ross (1968; cf Boyce 2015). Santa Rita would be the closest modern copper source to the project sites.

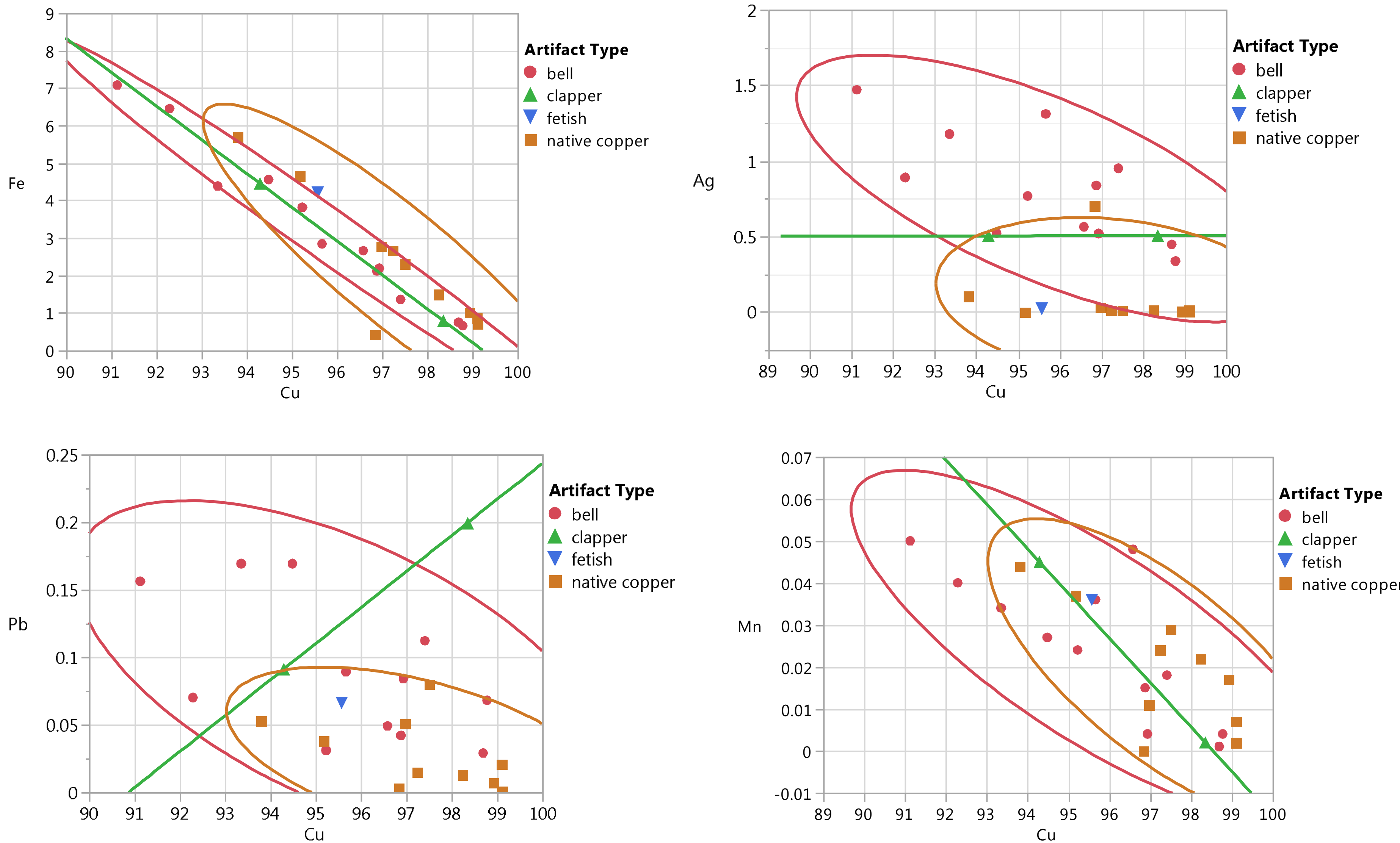

Figure 2. Mn, Fe, Ag, Pb versus Cu bivariate plots of the archaeological objects from Twin Pines and South Diamond Creek sites. Confidence intervals at 95%.

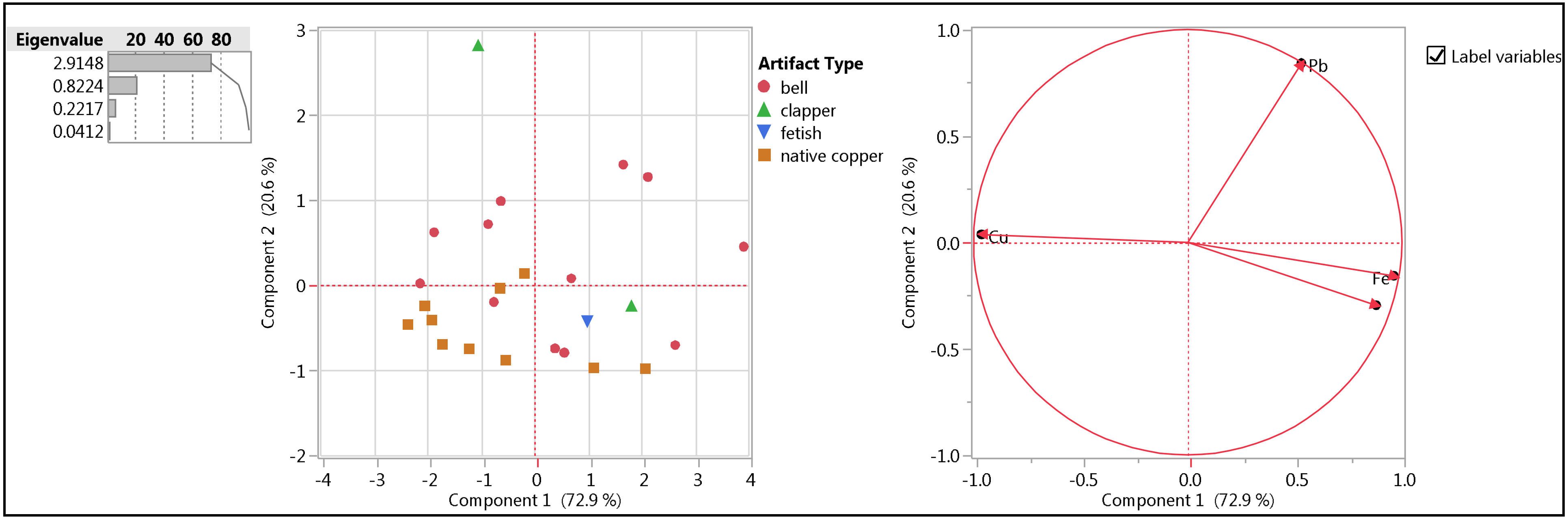

Figure 3. Principal components analysis using Mn, Fe, Cu, Pb as variables in the analysis from Table 1 (Eigenvalues suppressed). Component 1 at 72.9% is comprised of Mn, Fe, Pb and component 2 at 20.6% Cu. (see Table 1).

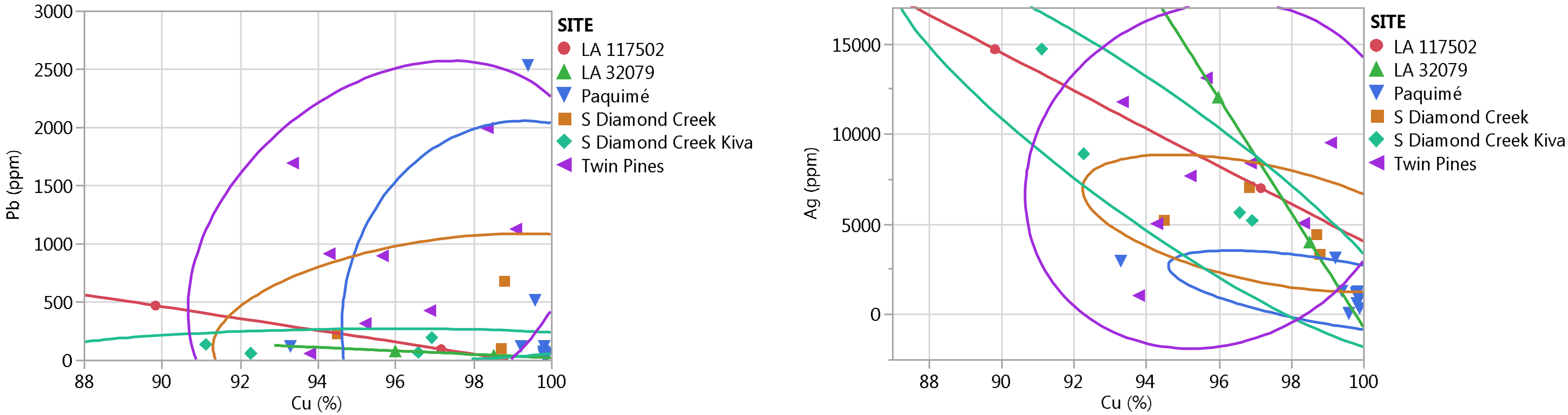

Figure 4. Pb and Ag versus Cu bivariate plots of the archaeological objects from the Mimbres sites, White Sands and Paquimé sites. Confidence intervals at 95%.

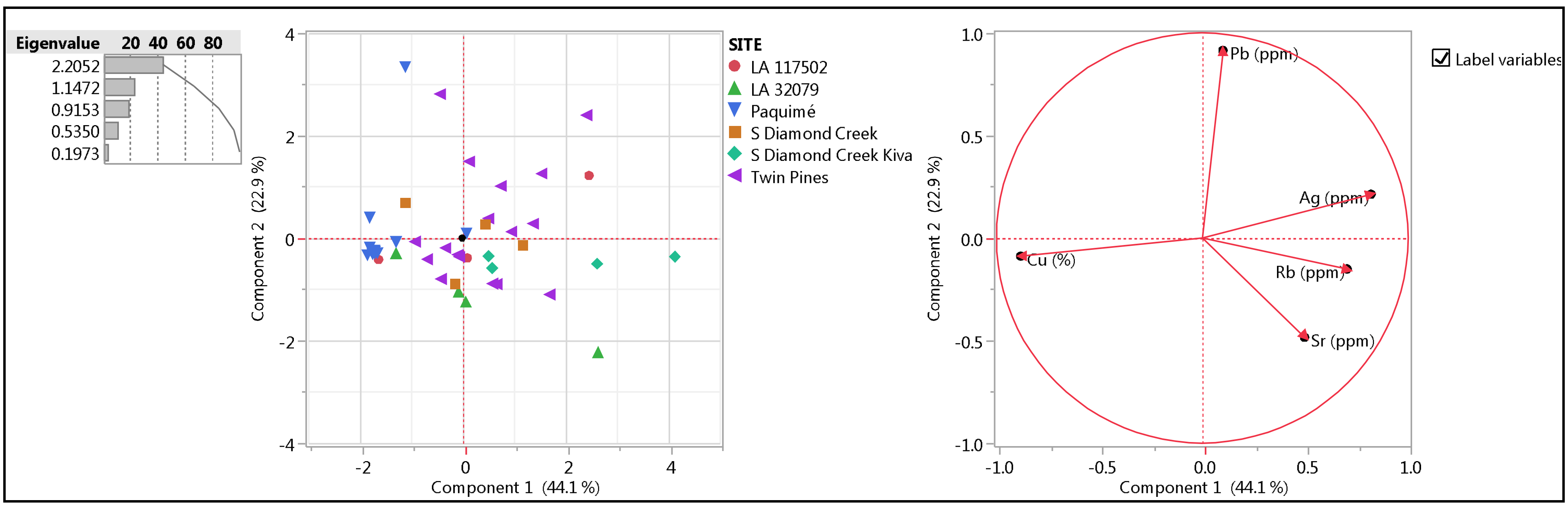

Figure 5. Principal components analysis using Mn, Fe, Cu, Pb as variables in the analysis of the Southwestern sites in Table 2 (see also Figure 4). Component 1 at 44.1% is comprised of Mn, Fe, Pb and component 2 at 22.9% Cu. (see Table 2). Note the greater elemental variability than in only the Mimbres sites (Figures 2 and 3).