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### Title

X-Ray Fluorescence (XRF) Analysis of Major Oxide and Trace Element Concentrations of Mainly Volcanic Rock Artifacts from Archaeological Sites in Central Arizona and Source Standards from the Picacho Mountains "Felsite" Quarry, AZ AA 3:65 (ASM), South...

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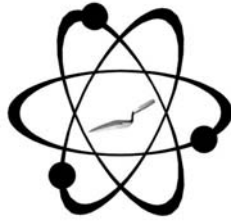
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**X-RAY FLUORESCENCE (XRF) ANALYSIS OF MAJOR OXIDE AND TRACE ELEMENT  
CONCENTRATIONS OF MAINLY VOLCANIC ROCK ARTIFACTS FROM  
ARCHAEOLOGICAL SITES IN CENTRAL ARIZONA AND SOURCE STANDARDS FROM  
THE PICACHO MOUNTAINS "FELSITE" QUARRY, AZ AA 3:65 (ASM), SOUTH CENTRAL  
ARIZONA**



Probable Cienega Large and San Pedro points from the collection of the I-10 project

by

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## INTRODUCTION

After the analysis of mainly volcanic rocks from the I-10, Ruthrauth-Prince project, it seemed possible that at least some of the raw materials could have been procured from the extensive volcanic rock quarries to the east in the Picacho Mountains, correctly termed "felsite" by Rachel Most during the Picacho Reservoir Archaic Project (Bayham et al. 1986; Most 1986; Shackley 2013). After a visual, compositional, and quantitative analysis of the rocks collected by Byl Bryce at the "felsite" quarries in October, 2013, it seems that at least some of the artifacts from the I-10 project could be produced from one of the chemical groups present at AZ AA:3:65 (ASM), the main quarry in the Picacho Mountains. These artifacts were not produced from the finer-grained gray raw material with a high-silica rhyolite composition, but the coarser grained dacite and lower silica rhyolite from that source.

## LABORATORY SAMPLING, ANALYSIS AND INSTRUMENTATION

All archaeological 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 2011a).

### Trace Element Analyses

Trace element analyses were conducted to provide data for future comparisons with sources that may be discovered at some point in time. All analyses for this study were conducted on a ThermoScientific *Quant'X* EDXRF spectrometer, located in 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

bremstrahlung, Rh target X-ray tube and a 76  $\mu\text{m}$  (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  $\text{l min}^{-1}$  Edwards vacuum pump, allowing for the analysis of lower-atomic-weight elements between sodium (Na) and titanium (Ti). 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 200 seconds livetime to generate x-ray intensity Ka-line data for elements titanium (Ti), manganese (Mn), iron (as  $\text{Fe}_2\text{O}_3^T$ ), 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. Trace element intensities were converted to concentration estimates by employing a least-squares 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 but Fe where a derivative fitting is used to improve the fit for iron and thus for all the other 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 2011a). Further details concerning the petrological choice of these elements in Southwest obsidians is available in Shackley (1988, 1995, 2005; also Mahood and Stimac 1991; 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 (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).

### **Major and Minor Oxide Analysis**

Analysis of the major and minor oxides of Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe is performed under the multiple conditions elucidated below. The composition of alkalis Na<sub>2</sub>O and K<sub>2</sub>O, and silica (SiO<sub>2</sub>) in these rocks allows for elemental determination of rock type (LeBas et al. 1986; Table 1 and Figure 1 here).

The 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 USGS RGM-1 obsidian standard (see also Shackley 2011a). The fundamental parameters (theoretical) method is run under conditions commensurate with the elements of interest and calibrated with four USGS standards (RGM-1, rhyolite; AGV-2, andesite; BHVO-1, hawaiite; BIR-1, basalt), and one Japanese Geological Survey rhyolite standard (JR-1).

## Conditions of Fundamental Parameter Analysis<sup>1</sup>

### Low Za (Na, Mg, Al, Si, P)

Voltage	6 kV	Current	Auto <sup>2</sup>
Livetime	100 seconds	Counts Limit	0
Filter	No Filter	Atmosphere	Vacuum
Maximum Energy	10 keV	Count Rate	Low

### Mid Zb (K, Ca, Ti, V, Cr, Mn, Fe)

Voltage	32 kV	Current	Auto
Livetime	100 seconds	Counts Limit	0
Filter	Pd (0.06 mm)	Atmosphere	Vacuum
Maximum Energy	40 keV	Count Rate	Medium

### High Zb (Sn, Sb, Ba, Ag, Cd)

Voltage	50 kV	Current	Auto
Livetime	100 seconds	Counts Limit	0
Filter	Cu (0.559 mm)	Atmosphere	Vacuum
Maximum Energy	40 keV	Count Rate	High

### Low Zb (S, Cl, K, Ca)

Voltage	8 kV	Current	Auto
Livetime	100 seconds	Counts Limit	0
Filter	Cellulose (0.06 mm)	Atmosphere	Vacuum
Maximum Energy	10 keV	Count Rate	Low

<sup>1</sup> 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.

<sup>2</sup> Current is set automatically based on the mass absorption coefficient.

The data from the WinTrace software were translated directly into Excel for Windows and SPSS software for statistical manipulation and the oxides plotted against the TAS plot to

determine rock type. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. RGM-1 a USGS rhyolite (obsidian) standard is analyzed during each sample run to check machine calibration (Table 1).

### **Analytic Trajectory**

In an effort to understand the rock types in the assemblage and the rock types and composition of the Picacho Mountains rock, the following analytic trajectory was followed. After acquiring the trace elements and oxides, the alkali/silica data for each artifact was calculated and "plotted" on the TAS plot (Figure 1). The rock type determination was then added in the rock type column in the spreadsheet and the spreadsheet loaded into SPSS for statistical analysis. An average linking Euclidean method hierarchical cluster analysis of Rb, Sr, Zr elements as variables for the artifacts and the sample of Picacho Mountains rocks was run to determine which of the artifacts were potentially nearest the Picacho Mountain samples based on the above incompatible elements (Figure 2). The artifacts that were clustered nearest the source rocks were examined to visually determine how close to the source composition that artifact clustered. It became immediately clear that the artifacts that were closest to source rocks were not the light gray high-silica rhyolitic composition source rocks, but the less silicic dacite and darker rhyolite rocks, and only four samples fit that category (Table 1 and Figure 3; see discussion below). Most of the Picacho Mountains source samples formed a separate group based on the elemental composition and were not likely to have been used to produce the artifacts (Figure 2).

## DISCUSSION

More than 61% of the raw material for tool production at these sites was determined to be rhyolite or a highly silicified rhyolite (>77% SiO<sub>2</sub>; Shackley 2013). A few of the artifacts were actually relatively low silica ultrabasic rocks such as foidite, phonolite, or phonotephrite, not an issue here. Interestingly, very few basalt rocks were used as raw materials, although there were quite a few relatively high silica intermediate rocks used to produce tools (dacite, andesite, trachyandesite, trachydacite). This would have been the few that could be from the Picacho Mountains quarry. The dominance of silicic volcanic rocks in the archaeological assemblage is likely due to the prevalence of rhyolites and high silica rhyolites in the mountains to the east of these sites up into Superior, Arizona, and the general lack of basic volcanic rocks such as basalt, in addition to the higher quality as a media for tool production for more silicic rocks (see Most 1986; Shackley 2011b). As geochemical investigations into volcanic raw materials increase in the Southwest, it is becoming increasingly evident that raw materials that have been called "basalt" in the past are actually dacite and related relatively high silica volcanic rocks (Shackley 2011b). Major sources of dacite used from Paleoindian through late periods include localities at the base of the Mogollon Rim in northern Arizona near Strawberry, and sources in northern New Mexico (Shackley 2011b). The I-10 archaeological assemblage appears to verify this procurement pattern.

While the artifacts at the Archaic sites at Picacho Reservoir appeared megascopically to be dominated by those produced by the local Picacho Mountains rock, compositional analysis, not common in archaeology at the time, was not attempted (Most 1986; Shackley 1986). The analysis of the Picacho Mountains rocks here is the first analysis of these raw materials. I was surprised given the amount of primary reduction at the Picacho Mountains sources witnessed by me in the 1980s, and Byl Bryce in 2013, that there would not be a better match between the I-10



artifacts and these sources. Geochemically, the probable magma mixing and hypabyssal formation of these "felsite" rocks in the Picacho Mountains, often derived from the granite/granitoid basement noted on the geologic map of the Picachos seems evident here (Richard et al. 1999). These aphyric to crystal poor felsic dikes and irregular pods are the rocks that were targeted by prehistoric knappers (Richard et al. 1999: 24-25). Richards et al. (1999) did not provide compositional analysis of these felsic rocks, but based on my observation and those of Bryce, are likely the dacite to rhyolite composition rocks discovered here.

Unfortunately, based on this analysis few of the artifacts from the I-10 project appear to be produced from Picacho Mountains rocks, but as noted earlier, there is abundant intermediate to silicic raw materials available in the immediate region. It would take a long-term geoarchaeological survey to discover these sources. The oxide and trace element analyses of the I-10 study could be used as a basis for that study.

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Table 1. Trace element concentrations for the source rocks from AZ AA:3:65 (ASM), selected oxide analyses of some of those rocks, and USGS RGM-1. Measurements in parts per million (ppm) or percent by weight as noted.

Sample	Ti ppm	Mn ppm	Fe ppm	Zn ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm	Ba ppm	Pb ppm	Th ppm
1	545	98	4717	17	180	74	20	69	16	204	20	26
2	670	120	5110	19	249	64	22	71	19	179	24	32
3	524	102	4868	13	194	86	19	67	16	180	20	23
4	605	108	4318	16	224	70	17	64	13	153	21	24
5	548	95	4332	10	157	81	17	61	14	209	17	20
6	658	100	5597	17	214	95	15	65	15	261	21	29
7	2406	371	22728	61	130	604	18	260	10	1504	20	11
8	1262	166	9614	19	173	270	21	128	9	990	17	15
9	2666	599	26006	59	97	560	17	265	14	1672	28	12
10	1444	291	11759	38	181	239	17	121	12	952	20	13
RGM1-S4	1582	284	13206	39	151	105	27	226	12	746	25	17
	Na2O %	MgO %	Al2O3 %	SiO2 %	Cl %	K2O %	CaO %	TiO2 %	V2O5 %	MnO %	Fe2O3 %	Σ
3	3.79	0	12.241	76.383	0	5.867	0.951	0.1	0	0	0.607	99.939
7	3.39	2.072	11.271	74.13	0.0492	2.6833	2.6682	0.402	0.0325	0.052	2.982	99.7322
8	3.179	0.543	13	74.091	0	5.482	1.815	0.195	0.012	0.011	1.523	99.851
9	3.486	2.446	14.323	68.61	0.021	3.178	3.437	0.477	0.004	0.142	3.575	99.699
RGM1-S4	3.855	0.025	12.328	74.312	0.049	5.13	1.523	0.279	0.017	0.049	2.279	99.846

Table 2. Selected artifacts probably produced from Picacho Mountain rock and the two source rocks most closely clustered and elementally similar.

Sample	Site (AZAA:12:)	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb	Source
1983	735	1289	247	12653	52	195	199	35	115	15	Picacho?
1196-4	735	1424	304	13970	39	161	206	32	122	14	Picacho?
1935-1	16	1288	325	13914	20	181	181	33	121	15	Picacho?
3000-1	90>	1350	307	14314	29	178	177	32	120	13	Picacho?
Picacho 7		1262	166	9614	19	173	270	21	128	9	source rock
Picacho 9		1444	291	11759	38	181	239	17	121	12	source rock

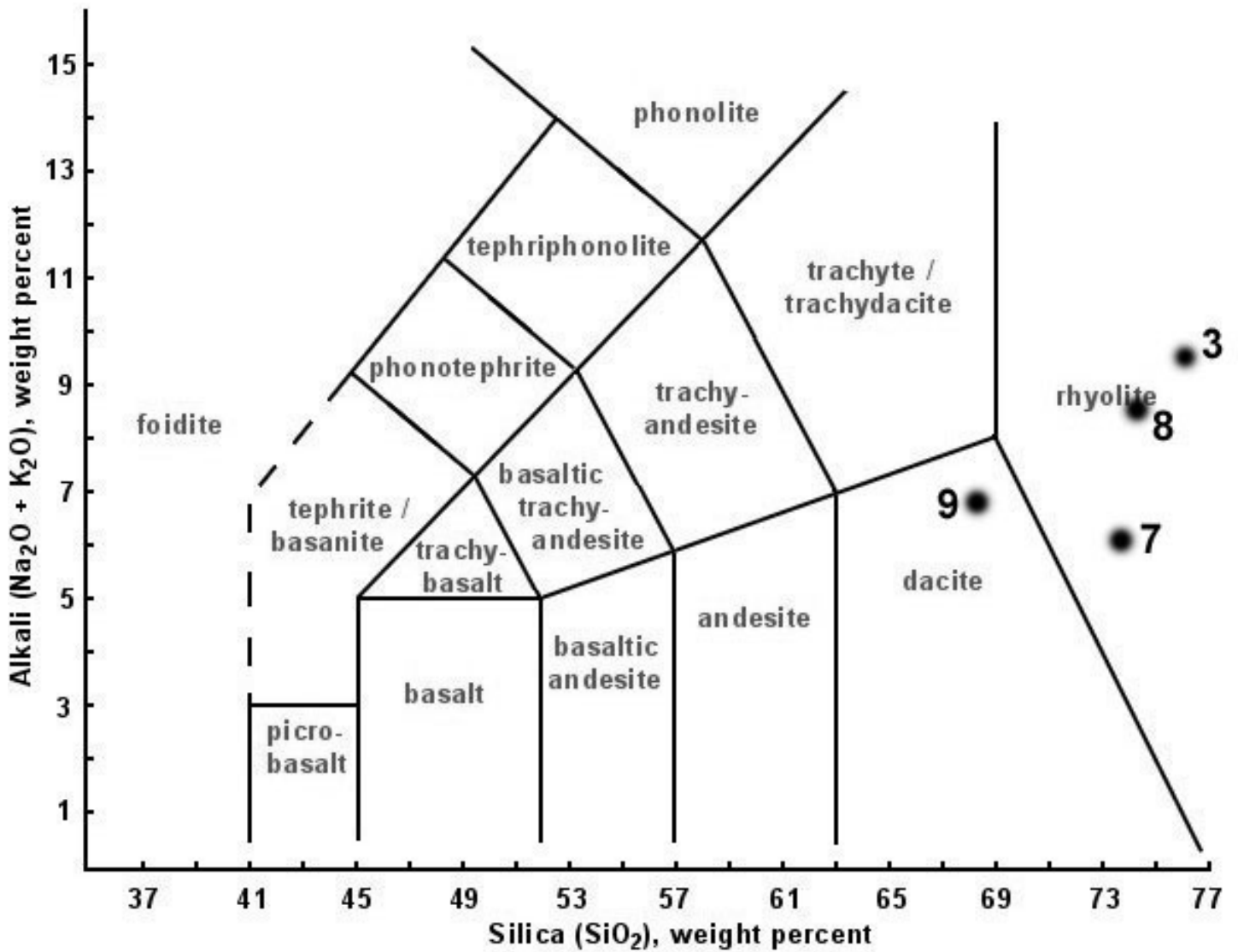


Figure 1. TAS plot used to determine rock type of samples similar to the four artifacts. (from LeBas et al. 1986). Samples 3 and 8 are the light gray felsic rocks common in Picacho Reservoir sites, but apparently not present in the I-10 assemblage (see Shackley 1986). Samples 7 and 9, most similar in trace composition to the four artifacts while differing in silica composition are quite similar in alkalis and trace composition, particularly uniquely high Ba (see Table 1).

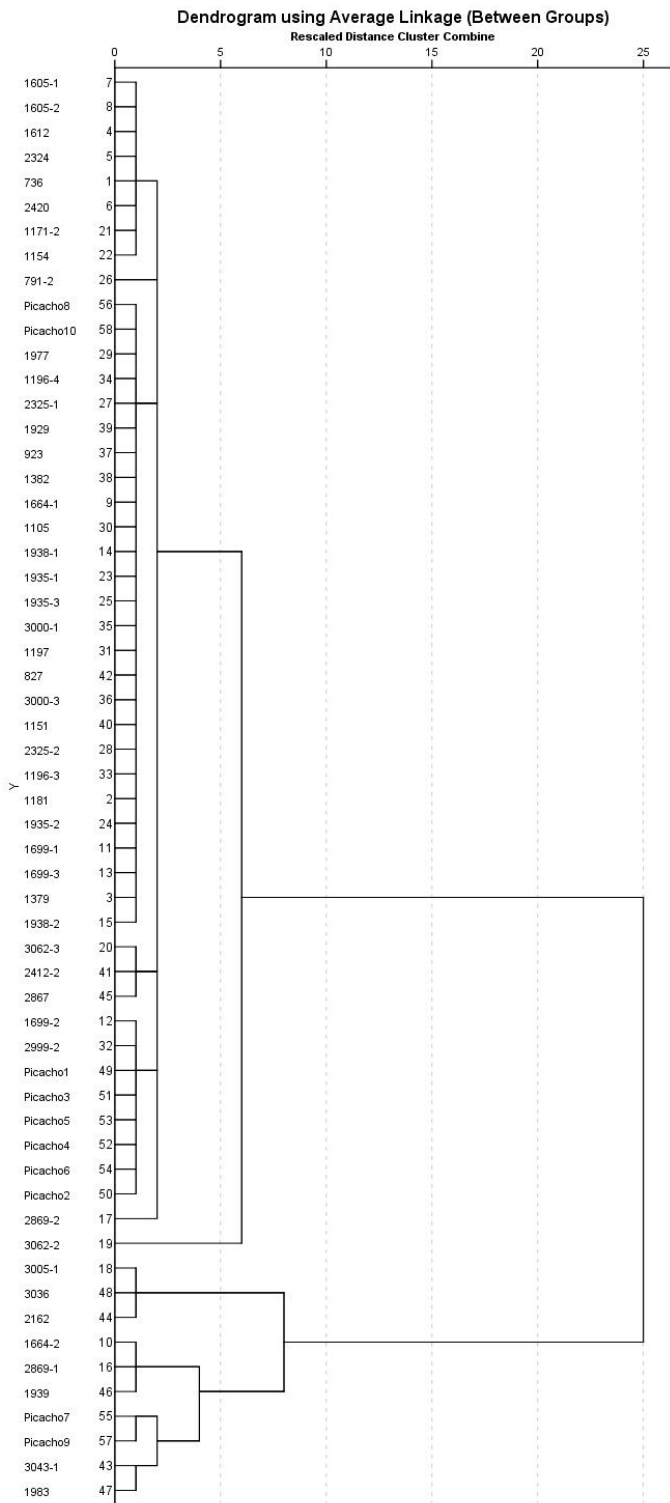


Figure 2. Average linkage method hierarchical cluster dendrogram of Rb, Sr, Zr data by artifact sample number, and Picacho Mountain source rock samples.

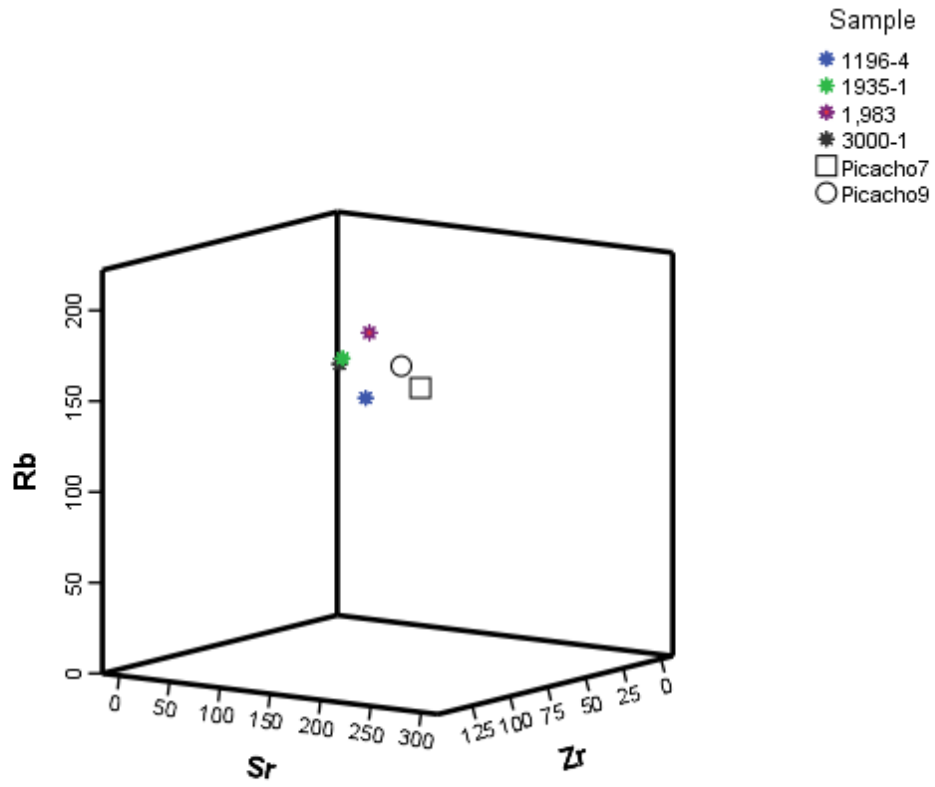


Figure 3. Three-dimensional plot of two of the Picacho Mountains source samples and the four artifacts closest in the cluster analysis.