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## Title

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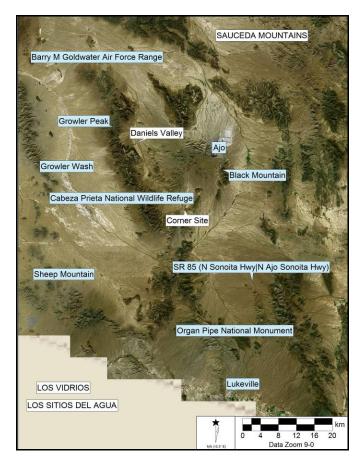
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GEOARCHAEOLOGICAL X-RAY FLUORESCENCE SPECTROMETRY LABORATORY 8100 WYOMING BLVD., SUITE M4-158

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#### SOURCE PROVENANCE OF OBSIDIAN ARTIFACTS FROM THE CORNER SITE AND DANIELS VALLEY, CABEZA PRIETA WILDLIFE REFUGE, SOUTHWESTERN ARIZONA



Satellite aerial orthophoto of the site locations, relevant obsidian sources (in capitals), and prominent features

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Report Prepared for U.S. Fish and Wildlife Service Cabeza Prieta National Wildlife Refuge Ajo, Arizona

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#### Introduction

The 22 obsidian artifacts, and one possible iron meteorite from two sites on Cabeza Prieta Wildlife Refuge, southwestern Arizona were produced from three of the sources previously recovered from sites on the refuge, Los Vidrios, Sonora (40.9%), Los Sitios del Agua (22.7%), and Sauceda Mountains (36.4%; see Shackley 2015, 2016, 2017; Table 1 and Figure 1 here). As in the previous study, the assemblage suggests that the local environment was important, with connections to the north and south apparent (see cover image). The composition of the high iron rock is similar to iron meteorites, although confirmation of this assignment is underway.

#### Laboratory Sampling, Analysis and Instrumentation

All archaeological and source 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).

#### Trace Element Analyses

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 bremsstrahlung, Rh target X-ray tube and a 76  $\mu$ 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 l min<sup>-1</sup> 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 100 seconds livetime to generate x-ray intensity  $K\alpha_1$ -line data for elements titanium (Ti), manganese (Mn), iron (as Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>), 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 quadratic 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. Further details concerning the petrological choice of these elements in Southwest obsidians is available in Shackley (1988, 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 (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).

The data from the WinTrace software were translated directly into Excel for Windows and SPSS (ver. 21) and JMP 12.0.1 software for statistical manipulation. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. RGM-1 a USGS obsidian standard was analyzed during each sample run for plutonic rock samples to check machine calibration (Table 1 and Figure 1). MBH Analytical leaded bronze standard 32XLB17 standard was used for the major and minor oxide analysis of the possible iron meteorite sample (Table 3 and Figure 2).

#### Major and Minor Oxide Analysis of Iron Rock

Analysis of the major oxides of Si, Al, Ca, Fe, K, Mg, Mn, Na, and Ti 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 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 11 USGS standards (RGM-1, rhyolite; AGV-2, andesite; BHVO-1, hawaiite; BIR-1, basalt; G-2, granite; GSP-2, granodiorite; BCR-2, basalt; W-2, diabase; QLO-1, quartz latite; STM-1, syenite), and one Japanese Geological Survey rhyolite standard (JR-1). See Lundblad et al. (2011) for another set of conditions and methods for oxide analyses.

#### 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 |
| Hi | igh 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   |
| Lo | ow Zb (S, Cl, K, C | a)            |              |        |
|    | Voltage            | 8 kV          | Current      | Auto   |

| Voltage        | 8 kV                | Current      | Auto   |
|----------------|---------------------|--------------|--------|
| Livetime       | 100 seconds         | Counts Limit | 0      |
| Filter         | Cellulose (0.06 mm) | Atmosphere   | Vacuum |
| Maximum Energy | v 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.

#### Discussion

As noted above, the vast majority of obsidian artifacts were produced from sources in the local region (northern Sonoran Desert). The direction of the sources, Los Sitios del Agua and Los Vidrios, Sonora to the south, and Sauceda Mountains to the north, indicates a concentration of local source procurement (Tables 1 and 2 and Figure 1; see cover image). All of the Sonoran Desert obsidian sources are generally equal media for tool production in quality and nodule size,

although Los Vidrios can be very brittle in hard hammer percussion, but equal to the others for

pressure work (Martynec et al. 2011; Shackley 2005).

One sample from Daniels Valley is not obsidian, but has the possible morphology and

composition that suggests it could be a meteorite (see http://meteorites.wustl.edu/metcomp/

;Table 3 and Figure 2 here). It is not certain and I have contacted EPS at Washington University

in St. Louis for confirmation.

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| Sample   | <b>Site</b><br>Daniels | Ті           | Mn         | Fe             | Zn        | Rb         | Sr       | Y        | Zr         | Nb       | Ва        | Source                                   |
|----------|------------------------|--------------|------------|----------------|-----------|------------|----------|----------|------------|----------|-----------|--|
| 1        | Valley<br>Daniels      | 1440         | 368        | 10804          | 48        | 161        | 78       | 33       | 212        | 20       | 1151      | Sauceda Mtns, AZ                         |
| 2        | Valley<br>Daniels      | 1646         | 418        | 11935          | 86        | 182        | 81       | 35       | 212        | 22       | 1117      | Sauceda Mtns, AZ<br>Los Sitios del Agua, |
| 3        | Valley<br>Daniels      | 1313         | 466        | 25098          | 188       | 149        | 16       | 85       | 727        | 51       | 76        | SON<br>Los Sitios del Agua,              |
| 4        | Valley<br>Daniels      | 1296         | 481        | 24650          | 172       | 152        | 19       | 82       | 729        | 54       | 67        | SON                                      |
| 5        | Valley<br>Daniels      | 1472         | 388        | 10851          | 72        | 167        | 75       | 31       | 202        | 25       | 1162      | Sauceda Mtns, AZ                         |
| 6        | Valley<br>Daniels      | 1554         | 410        | 11214          | 82        | 166        | 76       | 30       | 199        | 24       | 1117      | Sauceda Mtns, AZ                         |
| 7        | Valley<br>Daniels      | 1508         | 300        | 11109          | 75        | 161        | 105      | 31       | 182        | 16       | 970       | Sauceda Mtns, AZ                         |
| 8        | Valley<br>Daniels      | 1352         | 329        | 10154          | 58        | 148        | 72       | 32       | 187        | 17       | 1011      | Sauceda Mtns, AZ                         |
| 9        | Valley<br>Daniels      | 937          | 255        | 13104          | 113       | 272        | 20       | 71       | 225        | 31       | 14        | Los Vidrios, SON<br>Los Sitios del Agua, |
| 11       | Valley<br>Daniels      | 1328         | 483        | 23475          | 154       | 146        | 12       | 80       | 728        | 53       | 92        | SON                                      |
| 13       | Valley<br>Daniels      | 4749         | 11602      | 2116798        | 10        | 94         | 74       | 5        | 27         | 1        | 178       | not obsidian<br>Los Sitios del Agua,     |
| 14       | Valley<br>Daniels      | 1350         | 450        | 23423          | 168       | 147        | 18       | 78       | 722        | 54       | 74        | SON                                      |
| 15       | Valley<br>Daniels      | 964          | 271        | 12590          | 124       | 254        | 15       | 69       | 221        | 35       | 0         | Los Vidrios, SON                         |
| 16       | Valley<br>Daniels      | 888          | 265        | 13040          | 122       | 260        | 15       | 66       | 221        | 24       | 25        | Los Vidrios, SON                         |
| 17       | Valley<br>Daniels      | 921          | 250        | 12336          | 133       | 245        | 21       | 66       | 218        | 37       | 17        | Los Vidrios, SON                         |
| 18       | Valley<br>Daniels      | 1548         | 346        | 10718          | 49        | 162        | 72       | 32       | 205        | 27       | 1173      | Sauceda Mtns, AZ                         |
| 21       | Valley<br>Daniels      | 889          | 259        | 12273          | 123       | 243        | 17       | 69       | 221        | 33       | 26        | Los Vidrios, SON                         |
| 22<br>10 | Valley<br>Corner Site  | 1449<br>1048 | 353<br>293 | 10235<br>14256 | 52<br>153 | 150<br>280 | 67<br>16 | 34<br>74 | 191<br>230 | 25<br>35 | 1056<br>8 | Sauceda Mtns, AZ<br>Los Vidrios, SON     |
|          |                        |              |            |                |           |            |          |          |            |          |           |  |

Table 1. Elemental concentrations for the artifacts by site and USGS RGM-1 rhyolite standard.

| 12          | Corner Site<br>Daniels | 930  | 269 | 12393 | 122 | 245 | 12  | 73 | 217 | 31 | 39  | Los Vidrios, SON                         |
|-------------|------------------------|------|-----|-------|-----|-----|-----|----|-----|----|-----|--|
| 19          | Valley                 | 1118 | 293 | 14157 | 196 | 277 | 20  | 68 | 220 | 25 | 0   | Los Vidrios, SON<br>Los Sitios del Agua, |
| 20          | Corner Site            | 1274 | 431 | 22124 | 158 | 141 | 15  | 77 | 690 | 49 | 69  | SON                                      |
| 23<br>RGM1- | Corner Site            | 991  | 291 | 14357 | 155 | 281 | 15  | 73 | 228 | 30 | 0   | Los Vidrios, SON                         |
| S4<br>RGM1- |                        | 1527 | 285 | 13246 | 42  | 146 | 107 | 25 | 229 | 12 | 815 | standard                                 |
| S4          |                        | 1645 | 298 | 13134 | 44  | 143 | 106 | 28 | 219 | 9  | 835 | standard                                 |

|       |                |                 |                        | Source      |              |        |
|-------|----------------|-----------------|------------------------|-------------|--------------|--------|
|       |                |                 | Los Sitios del<br>Agua | Los Vidrios | Sauceda Mtns | Total  |
| Site  | Corner Site    | Count           | 1                      | 3           | 0            | 4      |
|       |                | % within Site   | 25.0%                  | 75.0%       | 0.0%         | 100.0% |
|       |                | % within Source | 20.0%                  | 33.3%       | 0.0%         | 18.2%  |
|       |                | % of Total      | 4.5%                   | 13.6%       | 0.0%         | 18.2%  |
|       | Daniels Valley | Count           | 4                      | 6           | 8            | 18     |
|       |                | % within Site   | 22.2%                  | 33.3%       | 44.4%        | 100.0% |
|       |                | % within Source | 80.0%                  | 66.7%       | 100.0%       | 81.8%  |
|       |                | % of Total      | 18.2%                  | 27.3%       | 36.4%        | 81.8%  |
| Total |                | Count           | 5                      | 9           | 8            | 22     |
|       |                | % within Site   | 22.7%                  | 40.9%       | 36.4%        | 100.0% |
|       |                | % within Source | 100.0%                 | 100.0%      | 100.0%       | 100.0% |
|       |                | % of Total      | 22.7%                  | 40.9%       | 36.4%        | 100.0% |

Table 2. Crosstabulation of obsidian source by site.

Table 3. Major, minor and trace elements for Sample 13, Daniels Valley.

| Sample            | Na2O      | MgO              | AI2O3            | SiO2             | P2O5             | K2O              | CaO              | TiO2             | V2O5                 | Cr2O3            | MnO              | Fe2O3     |           |                  |
|-------------------|-----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|----------------------|------------------|------------------|-----------|-----------|------------------|
|                   | %         | %                | %                | %                | %                | %                | %                | %                | %                    | %                | %                | %         |           |                  |
| 13                | 0.595     | 1.232            | 4.135            | 32.842           | 0                | 0.19             | 0.313            | 0.049            | 0                    | 0.018            | 0.671            | 59.729    |           |                  |
| 32XLB17           | 0         | 4.988            | 0.829            | 0.102            | 0                | 0                | 0                | 0                | 0                    | 0                | 0.353            | 0.843     |           |                  |
|                   |           |                  |                  |                  |                  |                  |                  |                  |                      |                  |                  |           |           |                  |
|                   |           |                  |                  |                  |                  |                  |                  |                  |                      |                  |                  |           |           |                  |
|                   | CI        | Co               | Ni               | Cu               | Zn               | Ga               | Rb               | Sr               | Y                    | Zr               | Nb               | Ва        | Pb        | Th               |
|                   | CI<br>ppm | <b>Со</b><br>ppm | <b>Ni</b><br>ppm | <b>Си</b><br>ppm | <b>Zn</b><br>ppm | <b>Ga</b><br>ppm | <b>Rb</b><br>ppm | <b>Sr</b><br>ppm | <b>Y</b><br>ppm      | <b>Zr</b><br>ppm | <b>Nb</b><br>ppm | Ba<br>ppm | Pb<br>ppm | <b>Th</b><br>ppm |
| 13                |           |                  |                  |                  |                  |                  |                  |                  | <b>Y</b><br>ppm<br>5 |                  |                  | -         |           |                  |
| 13<br>RGM1-<br>S4 | ppm       | ppm              | ppm              | ppm              | ppm              | ppm              | ppm              | ppm              | ••                   | ppm              |                  | ppm       | ppm       | ppm              |

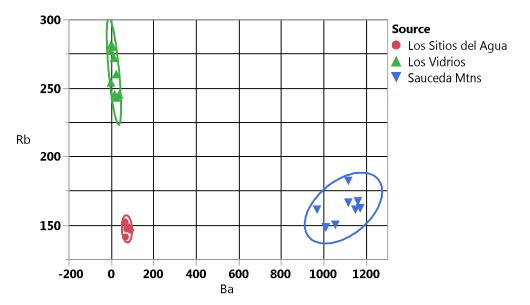


Figure 1. Ba/Rb bivariate plot of the archaeological obsidian samples. Confidence ellipses at 95%.

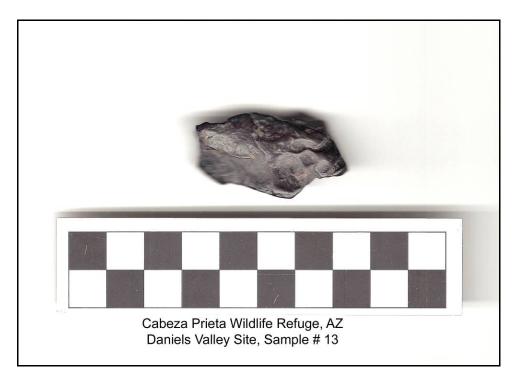


Figure 2. Possible meteorite sample (13) from Daniels Valley