Title
An Energy Dispersive X-Ray Fluorescence (EDXRF) Analysis of Obsidian Artifacts from CA-SDi-12,947/H, Pine Valley, San Diego County, California

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AN ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF) ANALYSIS OF OBSIDIAN ARTIFACTS FROM CA-SDI-12,947/H, PINE VALLEY, SAN DIEGO COUNTY, CALIFORNIA

by

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for

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28 September 1995
INTRODUCTION

The following report documents the EDXRF analysis of 9 obsidian artifacts from CA-SDI-12,947 in Pine Valley, eastern San Diego County, California. The obsidian assemblage is relatively diverse for this small sample with artifacts produced from obsidian procured from Imperial and Inyo Counties, California, and northern Baja California. The presence of Coso glass in the assemblage suggests the possibility of an Archaic period occupation in addition to the later ceramic period habitation.

ANALYSIS AND INSTRUMENTATION

All samples were analyzed whole, and were washed in distilled water before analysis. 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).

The trace element analyses were performed in the Department of Geology and Geophysics, University of California, Berkeley, using a Spectrace™ 400 (United Scientific Corporation) energy dispersive x-ray fluorescence spectrometer. The spectrometer is equipped with a Rh x-ray tube, a 50 kV x-ray generator, with a Tracor X-ray (Spectrace™) TX 6100 x-ray analyzer using an IBM PC based microprocessor and Tracor reduction software. The x-ray tube was operated at 30 kV, 0.20 mA, using a .127 mm Rh primary beam filter in a vacuum path at 250 seconds livetime to generate x-ray intensity Kα-line data for elements titanium (Ti), manganese (Mn), iron (as FeT), rubidium (Rb), strontium (Sr), ytrrium
(Y), zirconium (Zr), and niobium (Nb). Weight percent iron (Fe=Fe₂O₃T) can be derived by multiplying ppm estimates by 1.4297 \(10^{-4}\). Trace element intensities were converted to concentration estimates by employing a least-squares calibration line established for each element from the analysis of international rock standards certified by the US. Bureau of Standards, the US. Geological Survey, Canadian Centre for Mineral and Energy Technology, and the Centre de Recherches Pétrographiques et Géochimiques in France (Govindaraju 1989). Further detail concerning the petrological choice of these elements in Southwest obsidians is available in Shackley (1988, 1990, 1994, 1995; also Mahood and Stimac 1991; and Hughes and Smith 1993). Specific standards used for the best fit regression calibration for elements Ti through Nb include G-2 (basalt), AGV-1 (andesite), GSP-1 and SY-2 (syenite), BHVO-1 (hawaiite), STM-1 (syenite), QLM-1 (quartz latite), RGM-1 (obsidian), W-2 (diabase), BIR-1 (basalt), SDC-1 (mica schist), TLM-1 (tonalite), SCO-1 (shale), all US Geological Survey standards, and BR-N (basalt) from the Centre de Recherches Pétrographiques et Géochimiques in France (Govindaraju 1989). In addition to the reported values here, Ni, Cu, Zn, Pb, Ga, and Th were measured, but these are rarely useful in discriminating glass sources and are not reported. These data are available on disk by request.

The data from the Tracor software were translated directly into Quattro Pro for Windows software for manipulation and on into SPSS for Windows for statistical analyses. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. Table 1 shows a comparison between values recommended for two international obsidian and rhyolite rock standards, RGM-1, and NBS-278. One of these standards is analyzed during each sample run to check machine
calibration. The results shown in Table 1 indicate that the machine accuracy is quite high for the mid-Z incompatibles, and other instruments with comparable precision should yield comparable results.

Trace element data exhibited in Tables 1 and 2 are reported in parts per million (ppm), a quantitative measure by weight. Table 2 exhibits the trace element concentrations for the archaeological samples.

**DISCUSSION**

The dominance of Obsidian Butte material in the site is quite expectable given its relative proximity and the probable late occupation that appears to dominate the site (Hughes 1986; Hughes and True 1985; Table 2 and Figure 1 here). Yttrium was used as a discriminating element since it is quite high in Obsidian Butte as evident in Figure 1.

Three of the artifacts were produced from glass attributed to the San Felipe source in northern Baja California. This obsidian, while generally better for tool production, occurs as marekanites (Apache Tears) in relatively small nodules, and it’s presence in San Diego County seems to be restricted to the southern half. To my knowledge, San Felipe obsidian has only been recovered in late prehistoric contexts in San Diego County.

The presence of Coso glass here could indicate the presence of an Archaic component, and/or recycling of early obsidian by late occupants (Hughes and True 1985; Shackley 1990). It seems to be generally restricted to earlier components in southern California (Hughes and True 1985; Shackley 1993). The hydration data may shed some light on this issue.
REFERENCES CITED

Govindaraju, K.

Hampel, Joachim H.

Hughes, Richard E.


Hughes, Richard E., and Robert L. Smith

Hughes, R.E., and D.L. True

Mahood, Gail A., and James A. Stimac

McCarthy, J.J., and F.H. Schamber

Schamber, F.H.

Shackley, M. Steven


Table 1. X-ray fluorescence concentrations for selected trace elements of two international rock standards. ± values represent first standard deviation computations for the group of measurements. All values are in parts per million (ppm) as reported in Govindaraju (1989) and this study. RGM-1 is a U.S. Geological Survey rhyolite (obsidian) rock standard, and NBS-278 is a National Bureau of Standards obsidian standard.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Rb</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>Nb</th>
</tr>
</thead>
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<tr>
<td>RGM-1 (Govindaraju 1989)</td>
<td>1600</td>
<td>279</td>
<td>12998</td>
<td>149</td>
<td>108</td>
<td>25</td>
<td>219</td>
<td>8.9</td>
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<tr>
<td>RGM-1 (this study)</td>
<td>1513.2±46</td>
<td>232.8±15</td>
<td>13813±59</td>
<td>149.58±4.05</td>
<td>108.03±3</td>
<td>22.7±0.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBS-278 (Govindaraju 1468 1989)</td>
<td>402</td>
<td>14256</td>
<td>127.5</td>
<td>63.5</td>
<td>41</td>
<td>295</td>
<td>n.r.1</td>
<td></td>
</tr>
<tr>
<td>NBS-278 (this study)</td>
<td>1405±93</td>
<td>365±8</td>
<td>15399±394</td>
<td>130±2</td>
<td>68±2</td>
<td>43±1.7</td>
<td>290±4</td>
<td>18±2</td>
</tr>
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</table>

1 n.r = no report
Table 2. X-ray fluorescence concentrations for archeological samples from the archaeological specimens from SDI-12,947. All values are in parts per million (ppm).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Rb</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>Nb</th>
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<td>1</td>
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<td>1675.51</td>
<td>129.87</td>
<td>25.95</td>
<td>104.82</td>
<td>298.55</td>
<td>23.95</td>
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<td>2</td>
<td>882.41</td>
<td>236.95</td>
<td>10239.99</td>
<td>150.80</td>
<td>35.33</td>
<td>41.52</td>
<td>114.47</td>
<td>37.22</td>
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<td>3</td>
<td>716.87</td>
<td>209.54</td>
<td>8973.89</td>
<td>225.88</td>
<td>6.22</td>
<td>43.03</td>
<td>112.83</td>
<td>28.62</td>
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<tr>
<td>5</td>
<td>851.19</td>
<td>227.27</td>
<td>9655.01</td>
<td>1221.25</td>
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<td>259.96</td>
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<td>146.64</td>
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<td>345.02</td>
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<td>9</td>
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<td>10162.00</td>
<td>96.01</td>
<td>48.80</td>
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<td>96.01</td>
<td>48.80</td>
<td>13.46</td>
<td>73.41</td>
<td>0.00</td>
</tr>
</tbody>
</table>

1: Obsidian Butte  
2: San Felipe, BC  
3: Coso  
5: Coso  
6: San Felipe, BC  
8: Obsidian Butte  
10: Obsidian Butte  
12: Coso  
13: San Felipe, BC
Figure 1. Rb, Sr, Y three-dimensional plot of archaeological data.