Title
Energy-Dispersive X-Ray Fluorescence (XRF) Analysis of Trace Element Concentrations of Silicic Metavolcanic Rock Artifacts from 38FL425, South Carolina

Permalink
https://escholarship.org/uc/item/8ph1m204

Author
Shackley, M. Steven

Publication Date
2014-05-28

Supplemental Material
https://escholarship.org/uc/item/8ph1m204#supplemental

License
CC BY-NC 4.0
ENERGY-DISPERSIVE X-RAY FLUORESCENCE (XRF) ANALYSIS OF TRACE ELEMENT CONCENTRATIONS OF SILICIC METAVOLCANIC ROCK ARTIFACTS FROM 38FL425, SOUTH CAROLINA

Rhyolite Archaic point (sample #4, Bag 1410) from 38FL425

by

M. Steven Shackley Ph.D., Director
Geoarchaeological XRF Laboratory
Albuquerque, New Mexico

Report Prepared for

TRC
Columbia, South Carolina

28 May 2014
INTRODUCTION

The non-destructive whole rock analysis here of 29 archaeological specimens from 38FL425 in northern South Carolina indicates the procurement of stone raw materials from mainly high-silica metavolcanic rocks of Paleozoic age, many of which are most likely originally from the Uwharrie Mountains of the Carolina Slate Belt to the north in North Carolina, some of which were likely procured from the Great Pee Dee River alluvium nearby (Horton and Zullo 1991; Rogers 2006; see Shackley 2014). Compositional analysis of the tools from this site, including bifaces and fragments indicates that most of these artifacts were produced from raw materials that are compositionally similar to source samples submitted by Chris Young from Morrow Mountain State Park, Stanly County, North Carolina (MML sample numbers), and a locality near Asheboro, Randolph County, North Carolina (RLL sample numbers) likely both localities within Uwharrie Rhyolite. Similar to the Kolb Site analysis for Young, a site apparently upstream from this site, the assemblage appears to be debitage from tool production, biface preforms, and one finished, but fragmentary Archaic point (see illustration above; Shackley 2014).

In order to aid in the determination of the source of the raw materials from which the artifacts were produced, data from the earlier analysis of metavolcanic rock from the region was referenced (Glascock and Speakman 2006; see also Bondar 2001; Shackley 2014). A statistical analysis of the elemental composition was used to both characterize the artifacts and cobbles from the site, and compare to the source standards submitted by Young.

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 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 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 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 Fe$_2$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 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. 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 and other volcanic rocks 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).

The data from the WinTrace™ software were translated directly into Excel 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. RGM-1 a USGS obsidian standard is analyzed during each sample run for obsidian artifacts to check machine calibration (Table 1).

DISCUSSION

The analysis here was substantially augmented by the study of source standards from southern North Carolina submitted by Chris Young. In the previous analysis of artifacts from
the nearby Kolb Site, most of the artifacts were likely produced from an unknown source by comparison to the XRF results from the *Stone Quarries and Sourcing in the Carolina Slate Belt* that were used for comparison (Steponaitis et al. 2006; Glascock and Speakman 2006).

**Research Trajectory**

As in the Kolb Site study, a multivariate statistical analysis versus three-dimensional and bivariate plotting program was initiated. This has proven effective especially when the source is, in part, unknown (Glascock et al. 1998; Shackley 1998, 2007).

All samples were analyzed for trace elements Ti-Nb, Ba, Pb, Th (Table 1, Figures 1-5). Immediately apparent was that these rocks are likely highly metamorphosed rhyolites (metarhyolites) where some of the alkal-feldspars have changed to quartz during metamorphosis through what is often called greenschist facies metamorphism, but can occur through hydrothermal alteration during emplacement (Ehlers and Blatt 1982; Hatch et al. 1972). This process does not take much time geologically. In southern California and northern Baja California where I'm more familiar, the Santiago Peak Metavolcanic Province exhibits similar rocks metamorphosed in similar manner, but are Jurassic in age (Balch et al. 1984; Jones and Miller 1982). Hydrothermally altered rhyolites are favored raw materials during the Clovis period in New Mexico from the quarries near Socorro and have a very similar character to samples in this assemblage (Dello-Russo 2004), and fine-grained dacites in northern New Mexico were at times selected for point production during the Folsom period (Shackley 2011b). In all these cases, and presumably the Uwharrie rhyolites, metamorphism has produced an excellent raw material for stone tool production, but at a cost geoarchaeologically. Long-term metamorphism "scrambles" the geochemistry, and sometimes creates rather extensive elemental variability including increasing silica (SiO₂), such as the case here, and variable trace element...
composition from one area to another (see Bondar 2011 for a regional case and Shackley 2014 locally).

**Statistical versus Geological Interpretation**

In order to tease out any variability in this assemblage, a cluster analysis was first applied to the archaeological and Young source data using Fe, Zr, and Ba as variables which appeared to be most variable in the data and where elements are well above XRF detection limits. An average linking/squared Euclidean algorithm was used on the above variables in hierarchical cluster analysis (Figure 1). Cluster analysis is favored for geochemical data since it is often not multivariate normal and cluster analysis is not subject to non-normal issues (see Baxter 1992, 1994). Viewing the cluster dendrogram on the artifacts and source standards the clusters suggest that the vast majority of artifacts are similar to the North Carolina source data, with the exception of a fairly large group of high Fe samples that don't match the source data (Figure 1). This grouping is also reflected in Ba, Fe, Zr three-dimensional plots, and the Zr versus Fe bivariate plots (Figures 2-5).

Given the source data and artifact analysis it does appear that most of the artifacts were produced from some locality of Uwharrie Rhyolite quite possibly from the same source as the source rocks sampled from southern North Carolina. As at the Kolb Site most of the raw material used to produce these artifacts could very likely come from secondary deposits in and along the river. This has been seen throughout North America and easily seen with obsidian artifacts and elemental compositional analysis at sources and sites (Shackley 1989, 2005).

Finally, I strongly suggest reference to the Kolb Site study of Chris Young (Shackley 2014). Given the proximity of these two sites along the same drainage basin, and apparent similar chronology, much could be discerned. I have purposely not directly compared the data from these two sites. I leave that to you.
REFERENCES CITED

Balch, D.C., S.H. Bartling, and P.L. Abbott

Baxter, M.J.


Bondar, G.H.

Davis, K.D., T.L. Jackson, M.S. Shackley, T. Teague, and J.H. Hampel

Dello-Russo, R.D

Ehlers, E.G., and H. Blatt

Glascock, M.D., G.E. Braswell, and R.H. Cobean

Glascock, M.D., and R.J. Speakman

Govindaraju, K.
Hampel, Joachim H.  

Hatch, F.H., A.K. Wells, and M.K. Wells  

Hildreth, W.  

Horton, J.W., Jr., and V.A. Zullo  

Hughes, Richard E., and Robert L. Smith  

Jones, D.A., and R.H. Miller  

Mahood, Gail A., and James A. Stimac  

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

Rogers, J.W.  

Schamber, F.H.  

Shackley, M. Steven  


2014 *Energy-Dispersive X-Ray Fluorescence (XRF) Analysis of Major Oxide and Trace Element Concentrations of Silicic Metavolcanic Rock Artifacts from the Johannes Kolb Site (38DA75) Darlington County, South Carolina.* Report prepared for Chris Young, Department of Anthropology, Eastern New Mexico University, Portales.

Steponaitis, V.P., T.E. McReynolds, J.D. Irwin, and C.R. Moore (eds.)

Table 2. Elemental concentrations for the rock samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Zn</th>
<th>Rb</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>Nb</th>
<th>Ba</th>
<th>Pb</th>
<th>Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1160</td>
<td>246</td>
<td>1036</td>
<td>18</td>
<td>69</td>
<td>62</td>
<td>55</td>
<td>228</td>
<td>7</td>
<td>531</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>1179</td>
<td>242</td>
<td>1377</td>
<td>40</td>
<td>104</td>
<td>90</td>
<td>46</td>
<td>232</td>
<td>4</td>
<td>788</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>5556</td>
<td>1124</td>
<td>5418</td>
<td>94</td>
<td>118</td>
<td>162</td>
<td>36</td>
<td>198</td>
<td>10</td>
<td>900</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>984</td>
<td>292</td>
<td>9998</td>
<td>23</td>
<td>52</td>
<td>68</td>
<td>53</td>
<td>203</td>
<td>7</td>
<td>514</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>1529</td>
<td>163</td>
<td>4724</td>
<td>12</td>
<td>76</td>
<td>62</td>
<td>49</td>
<td>279</td>
<td>7</td>
<td>981</td>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>3931</td>
<td>817</td>
<td>4193</td>
<td>77</td>
<td>49</td>
<td>122</td>
<td>31</td>
<td>210</td>
<td>8</td>
<td>314</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>7</td>
<td>1141</td>
<td>310</td>
<td>9310</td>
<td>23</td>
<td>106</td>
<td>42</td>
<td>27</td>
<td>174</td>
<td>8</td>
<td>1009</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>1443</td>
<td>261</td>
<td>1440</td>
<td>37</td>
<td>52</td>
<td>73</td>
<td>51</td>
<td>252</td>
<td>9</td>
<td>634</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>1333</td>
<td>199</td>
<td>1022</td>
<td>25</td>
<td>46</td>
<td>55</td>
<td>54</td>
<td>251</td>
<td>9</td>
<td>420</td>
<td>22</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>1120</td>
<td>276</td>
<td>9037</td>
<td>43</td>
<td>96</td>
<td>44</td>
<td>40</td>
<td>159</td>
<td>6</td>
<td>709</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>11</td>
<td>768</td>
<td>253</td>
<td>8334</td>
<td>30</td>
<td>109</td>
<td>46</td>
<td>43</td>
<td>155</td>
<td>8</td>
<td>677</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>1230</td>
<td>136</td>
<td>8938</td>
<td>13</td>
<td>100</td>
<td>36</td>
<td>40</td>
<td>135</td>
<td>10</td>
<td>1053</td>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td>13</td>
<td>4695</td>
<td>876</td>
<td>5035</td>
<td>89</td>
<td>64</td>
<td>149</td>
<td>22</td>
<td>230</td>
<td>10</td>
<td>452</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>14</td>
<td>910</td>
<td>207</td>
<td>9340</td>
<td>32</td>
<td>63</td>
<td>59</td>
<td>48</td>
<td>201</td>
<td>13</td>
<td>428</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>15</td>
<td>5400</td>
<td>936</td>
<td>5501</td>
<td>96</td>
<td>123</td>
<td>96</td>
<td>21</td>
<td>226</td>
<td>12</td>
<td>722</td>
<td>21</td>
<td>8</td>
</tr>
<tr>
<td>16</td>
<td>811</td>
<td>117</td>
<td>3539</td>
<td>17</td>
<td>66</td>
<td>44</td>
<td>33</td>
<td>135</td>
<td>9</td>
<td>552</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>17</td>
<td>838</td>
<td>175</td>
<td>6875</td>
<td>17</td>
<td>79</td>
<td>65</td>
<td>44</td>
<td>158</td>
<td>9</td>
<td>682</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>18</td>
<td>1290</td>
<td>238</td>
<td>1275</td>
<td>23</td>
<td>90</td>
<td>48</td>
<td>39</td>
<td>182</td>
<td>12</td>
<td>828</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>19</td>
<td>1492</td>
<td>412</td>
<td>1919</td>
<td>35</td>
<td>61</td>
<td>56</td>
<td>68</td>
<td>296</td>
<td>10</td>
<td>664</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>20</td>
<td>4342</td>
<td>1053</td>
<td>3479</td>
<td>68</td>
<td>72</td>
<td>90</td>
<td>39</td>
<td>169</td>
<td>9</td>
<td>389</td>
<td>18</td>
<td>7</td>
</tr>
<tr>
<td>21</td>
<td>1089</td>
<td>209</td>
<td>9617</td>
<td>29</td>
<td>74</td>
<td>57</td>
<td>47</td>
<td>237</td>
<td>15</td>
<td>1085</td>
<td>8</td>
<td>19</td>
</tr>
<tr>
<td>22</td>
<td>4199</td>
<td>1379</td>
<td>6022</td>
<td>94</td>
<td>17</td>
<td>316</td>
<td>37</td>
<td>208</td>
<td>17</td>
<td>275</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>23</td>
<td>5466</td>
<td>1309</td>
<td>6998</td>
<td>78</td>
<td>74</td>
<td>368</td>
<td>16</td>
<td>50</td>
<td>5</td>
<td>263</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>24</td>
<td>1233</td>
<td>322</td>
<td>1035</td>
<td>21</td>
<td>200</td>
<td>43</td>
<td>35</td>
<td>148</td>
<td>7</td>
<td>845</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>25</td>
<td>1202</td>
<td>221</td>
<td>1117</td>
<td>51</td>
<td>73</td>
<td>63</td>
<td>54</td>
<td>233</td>
<td>7</td>
<td>682</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>26</td>
<td>2025</td>
<td>473</td>
<td>1877</td>
<td>47</td>
<td>39</td>
<td>103</td>
<td>52</td>
<td>240</td>
<td>11</td>
<td>881</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>27</td>
<td>2352</td>
<td>646</td>
<td>1996</td>
<td>60</td>
<td>146</td>
<td>106</td>
<td>44</td>
<td>212</td>
<td>12</td>
<td>2046</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>28</td>
<td>1230</td>
<td>318</td>
<td>2057</td>
<td>38</td>
<td>66</td>
<td>65</td>
<td>54</td>
<td>239</td>
<td>5</td>
<td>518</td>
<td>23</td>
<td>17</td>
</tr>
<tr>
<td>29</td>
<td>371</td>
<td>118</td>
<td>2821</td>
<td>10</td>
<td>&lt;1</td>
<td>3</td>
<td>6</td>
<td>11</td>
<td>2</td>
<td>123</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>RGM1-S4</td>
<td>1452</td>
<td>281</td>
<td>1292</td>
<td>41</td>
<td>149</td>
<td>102</td>
<td>23</td>
<td>219</td>
<td>11</td>
<td>813</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>RGM1-S4</td>
<td>1517</td>
<td>291</td>
<td>1292</td>
<td>35</td>
<td>148</td>
<td>104</td>
<td>25</td>
<td>222</td>
<td>5</td>
<td>847</td>
<td>24</td>
<td>21</td>
</tr>
</tbody>
</table>
Figure 1. Average linking, hierarchical cluster dendrogram based on Fe, Zr, Ba of 38FL425 artifacts and the Chris Young source data (MML; RLL). First 29 number are artifact sample numbers.
Figure 2. Ba, Fe, Zr three-dimensional plot of the artifacts only. Numbers correspond to sample numbers.
Figure 3. Ba versus Zr bivariate plot of the artifacts only including sample numbers. Compare to Figure 2. Note the grouping of samples with highest Fe, the same as the unique cluster in the cluster analysis (Figure 1).
Figure 4. Ba, Fe, Zr three-dimensional plot the same as in Figure 2 with Young source standards. Outlier samples noted with sample numbers.
Figure 5. Zr versus Fe bivariate plot, the same plot as in Figure 3 with Young source standards plotted. Again, note high Fe outlier group identified in cluster analysis (Figure 1).