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AN ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF) ANALYSIS OF A SAMPLE OF OBSIDIAN ARTIFACTS FROM INDIAN HILL ROCKSHELTER, EAST SAN DIEGO COUNTY, CALIFORNIA

by

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INTRODUCTION

The following is a report of a x-ray fluorescence reanalysis of 19 obsidian artifacts recovered from Indian Hill Rockshelter (SDi-2537), eastern San Diego County, California. The analysis is a check on the previous analysis indicating the possibility of unknown source provenience for some of the samples in the assemblage (Bouey 1992). This analysis indicates that all the material can be assigned to source, although the small sample sizes of many of the samples precludes a confident source assignment by EDXRF (see Jackson and Hampel 1992). As with the earlier analysis the material appears to be derived from the two closest known sources Obsidian Butte to the east and San Felipe (Arroyo Matomí) in northeaster Baja California Norte.

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 440 (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, .20 mA, using a .127 mm Rh primary beam filter in a vacuum path at 250 seconds livetime to generate x-ray intensity $K\alpha$-line data for elements titanium (Ti), manganese (Mn), iron (as Fe^T), rubidium (Rb), strontium

(Sr), yttrium (Y), zirconium (Zr), and niobium (Nb). Weight percent iron ($Fe=Fe_2O_3^T$) can be derived by multiplying ppm estimates by 1.431 (Glascock 1991). Trace element intensities were converted to concentration estimates by employing a least-squares calibration line established for each element from the analysis of up to 26 international rock standards certified by the U.S. Bureau of Standards, the U.S. Geological Survey, Canadian Centre for Mineral and Energy Technology, and the Centre de Recherches Pétrographiques et Géochimiques in France (Govindaraju 1989). Further details concerning the petrological choice of these elements in Southwest obsidians is available in Shackley (1988, 1990; also Mahood and Stimac 1991).

The data from the Tracor software were translated directly into Quattro Pro 4.0 software for manipulation and on into SPSSPC+ 3.0 for statistical analyses. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards. Table 1 shows a comparison between values recommended for two international rock standards, one rhyolite (RGM-1) and one obsidian (NBS-278). One of these standards is analyzed during each sample run to insure continued machine calibration. The results shown in Table 1 indicate that the machine accuracy is quite high, 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. Source probability is based on a comparison with 1-sigma level of variability. Table 2 exhibits the trace element concentrations for the 19 samples. Source standard data for Obsidian Butte can be found in Hughes (1986). San Felipe source standard data is, as yet, unpublished (Shackley et al. 1993; but see Bouey 1984 for semi-quantitative data). Figures 1 through 4 display bivariate plots of the data using five of the measured elements.

DISCUSSION

The EDXRF analysis here is essentially similar to that performed by Bouey using the Kevex instrument at the University of California, Davis (Bouey 1992). Further sampling at the source and more intensive XRF analyses allow for more confident assignment to the San Felipe source in Baja California (see Table 3). The small size of many of the debitage pieces, however, precludes confident source assignment.

The presence of San Felipe glass in San Diego County sites is apparently a rather rare occurrence (Banks 1971; Bouey 1984; Douglas 1981). This is probably mainly due to distance-to-source issues, but this is rarely the only cause. As a raw material it is superior to Obsidian Butte glass, but is available only as small marekanites, generally less than 5 cm in maximum diameter (Douglas 1981). This nodule size difference, coupled with the "distance-to-source" problem, and possibly cultural control of the source, are the likely factors influencing the general rarity of this source material in San Diego County sources. The relatively high proportion of San Felipe derived glass in this assemblage is probably due to proximity. McDonald suggests that its position in the column in the upper levels argues for a late introduction in the area and "might only represent several isolated articles that reached the area from San Felipe" (1992:107). This is probably the case although the small nodule size available generally precludes the production of more than one or possibly two points from one nodule (Shackley 1990).

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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. Element-to-Oxide conversions from Glascock (1991).

SAMPLE	Ti	Mn	Fe	Rb	Sr	Y	Zr	Nb
RGM-1 (Govindaraju 1989)	1600	279	12998	149	108	25	219	8.9
RGM-1 (this study)	1513.24±46	232.86±15	13813±59	149.58±4.05	108.03±3	22.7±.86	226.8±2	10±.28
NBS-278 (Govindaraju 1989)	1468	402	14256	127.5	63.5	41	295	n.r.[1]
NBS-278 (this study)	1405±93	365±8	15399±394	130±2	68±2	43±1.7	290±4	18±2

[1] n.r = no report

Table 2. X-ray fluorescence concentrations for selected elements for obsidian artifacts from Indian Hill Rockshelter. All measurements in parts per million (ppm).

SAMPLE	Ti	Mn	Fe	Rb	Sr	Y	Zr	Nb	Source
D557F	1182.3	166.3	9481.6	117.8	31.2	21.7	67.7		San Felipe*
D689C	635.5	152.1	9978.3	149.6	36.1	28.1	94.2	7.347	San Felipe
D6110	1890.0	177.1	10263.6	152.2	38.3	34.6	113.9	7.649	San Felipe
B578	764.9	176.6	9021.4	134.1	28.4	28.2	95.2	7.202	San Felipe
C568	1221.7	188.5	12078.9	156.3	35.7	29.4	101.2	2.947	San Felipe
D5187C	819.3	195.1	9947.1	137.9	34.7	27.2	108.4	7.253	San Felipe
D669E	1700.4	248.5	18493.5	113.4	27.2	62.8	193.2	22.29	Obsidian Butte
P735	823.7	250.6	12605.2	155.5	61.9	33.7	125.3	9.468	San Felipe
D689D	780.4	98.6	5974.1	69.8	12.9	22.5	59.7	0.0	San Felipe*
D557E	1388.2	187.0	10590.0	129.7	32.4	27.4	79.2	7.491	San Felipe
D515C	1053.1	221.9	9534.7	88.6	38.7	25.1	79.7	5.837	San Felipe*
D5199B	1330.3	160.8	8320.8	83.8	33.7	17.9	68.8	1.234	San Felipe*
D557D	971.7	118.0	7210.5	98.0	17.4	20.6	58.5	0.0	San Felipe
D6106D	1141.2	286.7	15198.4	100.9	6.91	81.6	191.4	9.379	Obsidian Butte
C7130	908.5	211.7	10909.4	131.2	61.5	34.1	109.8	6.295	San Felipe
B426	830.3	169.2	10013.0	151.6	44.4	33.5	114.5	1.945	San Felipe
D574D	1289.9	254.2	12127.3	146.7	30.1	24.9	101.6	0.0	San Felipe
D574E	1268.1	152.7	9989.9	96.8	42.0	23.3	66.3	0.0	San Felipe
D574F	1065.6	104.9	7853.4	97.47	32.2	23.4	66.0	10.4	San Felipe

* Sample very small increasing the chance for analytic error (Jackson and Hampel 1992).

Table 3. Central tendency statistics for obsidian source standards from Arroyo Matomí (San Felipe), Baja California Norte. Analytic and instrument settings described in Shackley (1991, 1992).

Element	Mean	Std Dev	Minimum	Maximum	N
Ti	723.45	181.26	521.8	1129.9	8
Mn	208.76	15.70	194.6	244.3	8
Fe	11795.46	492.58	11217.5	12879.6	8
Rb	115.36	13.39	105.7	146.9	8
Sr	42.24	9.70	37.1	66.0	8
Y	34.15	3.81	28.9	39.5	8
Zr	144.05	11.61	134.8	171.6	8
Nb	10.80	2.90	4.5	14.4	8

Figure 1. Fe versus Zr concentration plot for obsidian artifacts from SDi-12809 (O=Obsidian Butte; S=San Felipe).

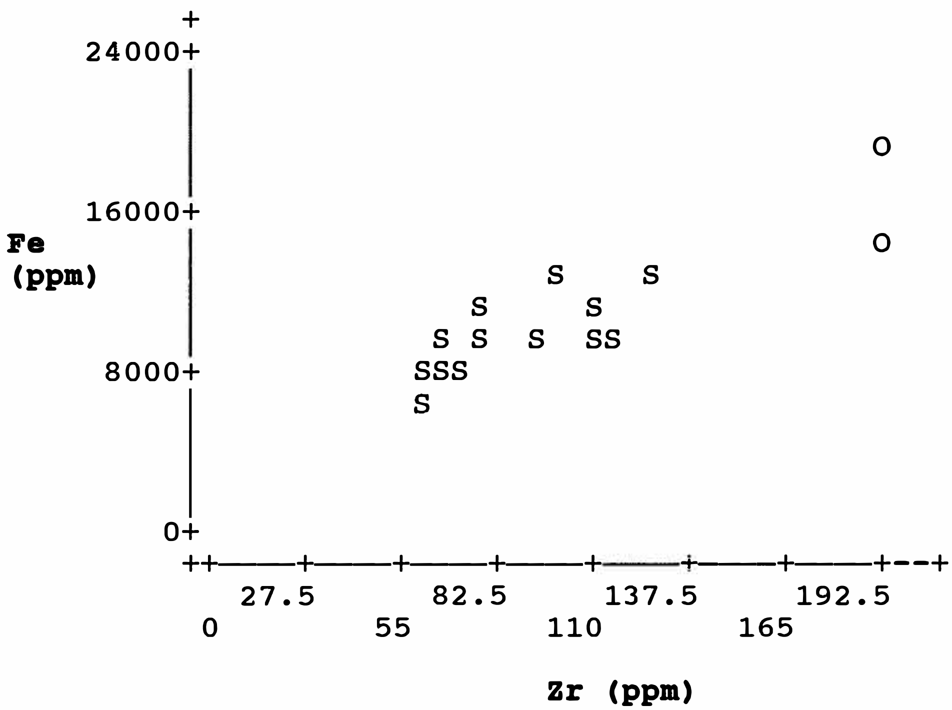

Figure 2. Y versus Zr concentration plot for obsidian artifacts from SDi-12809 (O=Obsidian Butte; S=San Felipe).

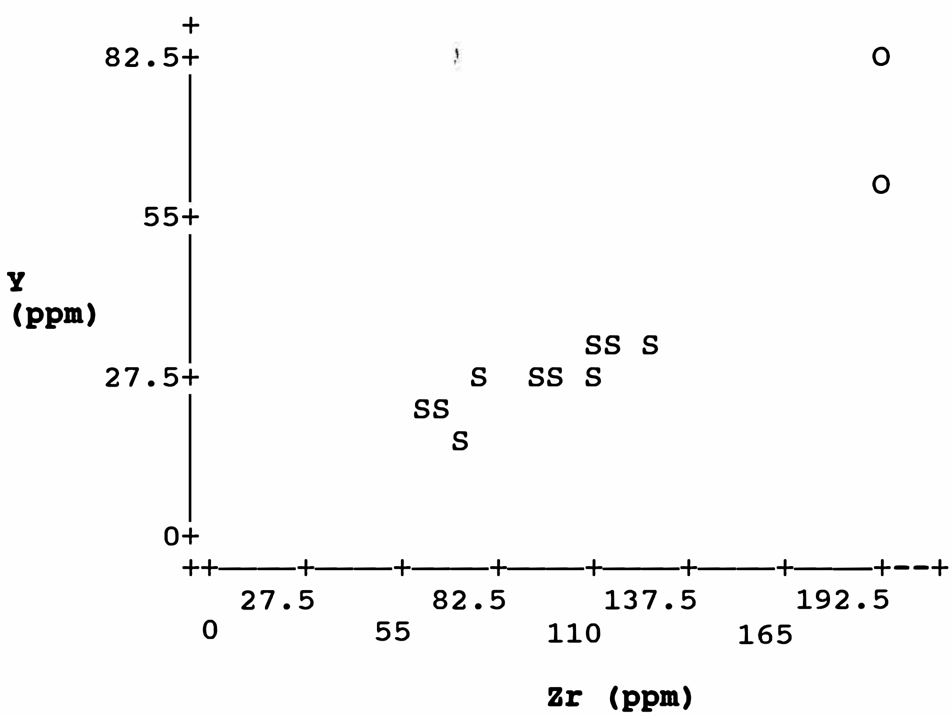

Figure 3. Sr versus Zr concentration plot for obsidian artifacts from SDi-12809 (O=Obsidian Butte; S=San Felipe).

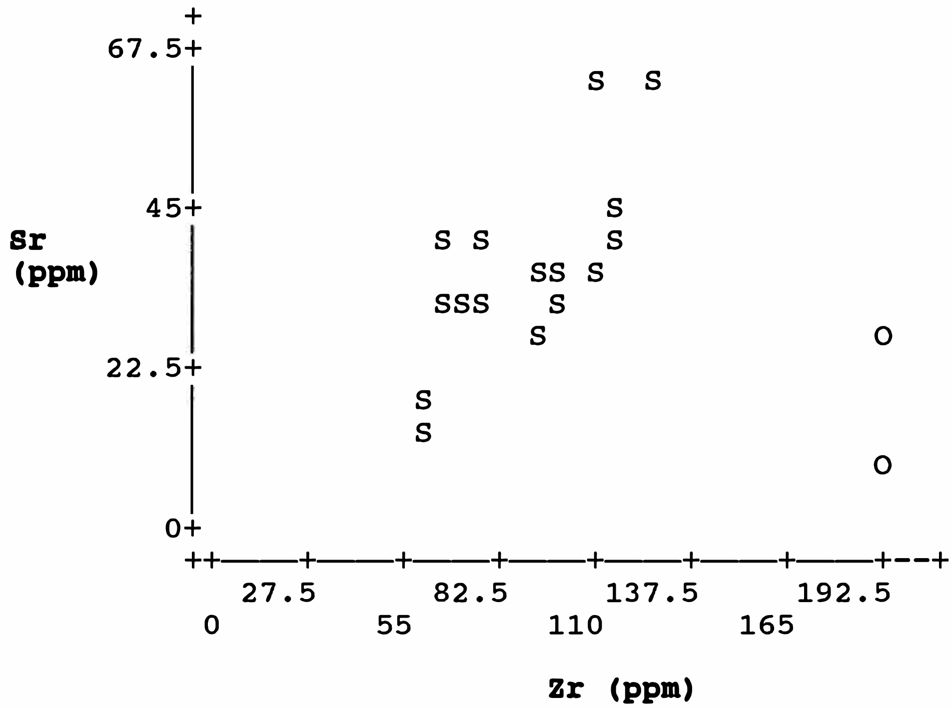

Figure 4. Rb versus Zr concentration plot for obsidian artifacts from SDi-12809 (O=Obsidian Butte; S=San Felipe).