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Trace Element Composition of Obsidian Butte, Imperial County, California

Richard E. Hughes

*Anthropological Studies Center, Sonoma State University,
Rohnert Park, California 94928*

Abstract.—Non-destructive energy dispersive x-ray fluorescence analyses were performed on rhyolitic volcanic glass (obsidian) from Obsidian Butte, located at the south end of the Salton Sea in Imperial County, California. Sixteen trace and rare earth element concentrations were measured in parts per million (ppm), and these values compared favorably with analyses employing destructive techniques. The results of the present study demonstrate that archaeological artifacts can be matched reliably to the Obsidian Butte source on the basis of non-destructive quantitative analysis, facilitating the study of prehistoric Southern California obsidian trade and interlaboratory comparison of analytical results.

Obsidian has long been of interest to archaeologists because in regions where it occurs it was the raw material preferred for the manufacture of prehistoric chipped stone tools. Recently, techniques from the physical sciences have provided new ways of deriving information from obsidian artifacts. Using x-ray fluorescence or neutron activation techniques, it is possible to determine the trace and rare earth element composition of volcanic glass (obsidian), and to distinguish between parent geological sources on the basis of contrasts in these elemental constituents. Once the trace element configurations (or "profiles") for obsidian sources in a region are established, it is possible to analyze artifacts from archaeological sites and match them with known obsidian sources on the basis of trace and rare earth element similarities. This procedure, popularly known as "fingerprinting," has been profitably applied to studies of prehistoric trade in western North America (e.g., Jack and Carmichael 1969; Jackson 1974; Jack 1976; Hughes 1983a, b, 1984; Ericson 1981; Nelson 1984).

However, until quite recently, comparatively little research on obsidian trade has been conducted in southern California in part because of the absence of a published quantitative obsidian source data base. Trace and rare earth concentration values have been published for some elements (see Ericson 1981:10; Robinson et al. 1976:table 2), but these have been derived from destructive analyses (i.e., those necessitating crushing and powdering some portion of the sample), which have obvious drawbacks for archaeological studies because of the desirability of analyzing artifacts without sacrificing some portion of them for study. The purposes of this study are to present a series of quantitative trace and rare earth element measurements for Obsidian Butte glass using non-destructive x-ray fluorescence, to compare these values with those generated from previous analyses conducted using destructive methods, and to illustrate the benefits of non-

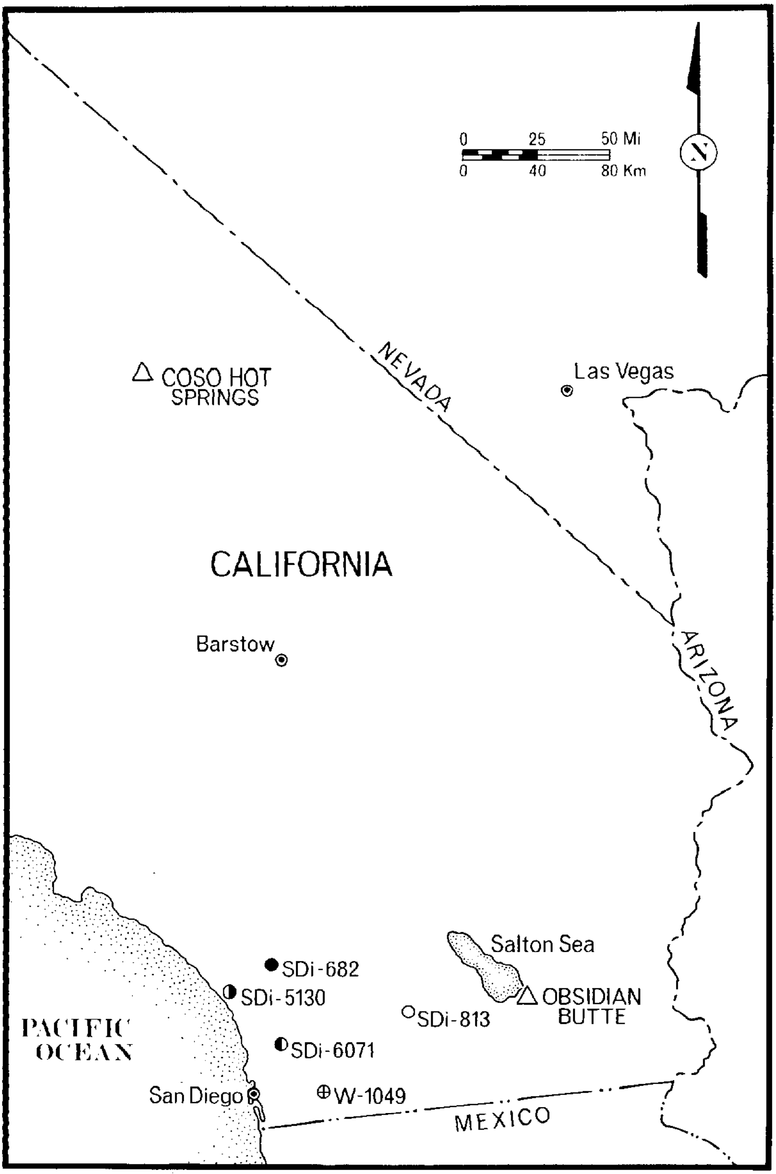

Fig. 1. Map of southern California showing the locations of obsidian sources utilized during prehistoric times (open triangles) and archaeological sites (filled dots) discussed in the text.

destructive quantitative analysis for the study of prehistoric obsidian trade in southern California.

The Setting

The presence of rhyolitic obsidian at Obsidian Butte has been known to geologists for some time (e.g., Rogers 1934; Kelley and Soske 1936). However, Obsidian Butte (Fig. 1) was first brought to the attention of the archaeological community by Treganza (1942:155, fn. 13) and Heizer and Treganza (1944:305), who noted abundant evidence for its use during prehistoric times as a quarry source for obsidian tools. More than two decades later, Ericson et al. (1976:222) provided a more detailed description of the immediate geological context. Obsidian Butte is actually only one of four volcanoes (Obsidian Butte, Red Island, Rock Hill, and Mullet Island) in the vicinity of the Salton Buttes (see Robinson et al. 1976: fig. 2) where Quaternary volcanic activity produced rhyolitic obsidian and pumice. However, petrochemical analyses indicates no systematic elemental variation between these rhyolitic domes (Robinson, et al. 1976:354). K-Ar ages of ca. 16,000 B.P. (Muffler and White 1969:162) and 33,000 ± 35,000 B.P. (2 σ) (Friedman and Obradovich 1981:40–41) have been reported for Obsidian Butte obsidian.

Methods

To determine whether non-destructive analysis could yield quantitative elemental measurements comparable to those previously published using more time consuming, destructive techniques, analyses were conducted on a sample of 10 unmodified obsidian flakes collected from the southeast side of Obsidian Butte in T11S, R13E, NE ¼ of the NW ¼ of the SE ¼ of Section 32, as depicted on the USGS Obsidian Butte, Calif., 7.5′ series quadrangle (1956). No special sample preparation was made, other than rinsing each specimen in distilled water to remove surface contaminants that might effect the analysis.

Laboratory analyses were conducted by the author at the Department of Geology and Geophysics, University of California, Berkeley, on a Spectrace 440 (United Scientific Corporation) energy dispersive x-ray fluorescence machine equipped with a 572 power supply (50 kV, 1 mA), 534-1 pulsed tube control, 588 bias/protection module, 514 pulse processor (amplifier), Tracor Northern 1221 100 mHz analog to digital converter, a Tracor Northern 2000 computer based analyzer with a LSI-11 microcomputer with 24k word capacity, and a Si(Li) solid state detector with 142 eV resolution (FWHM) at 5.9 keV in a 30 mm^2 area. Trace element analyses in the 5–25 keV region of the energy spectrum were conducted using a Rh x-ray tube operated at 30.0 kV, .40 mA pulsed with a .04 mm Rh primary beam filter, while analyses in the 20-60 keV region were conducted using an Am241 100 mCi radioisotope (see Hughes 1983a:fig. 2). All analyses were conducted at 200 seconds livetime. NI (Kα), Cu (Kα), Zn (Kα), Ga (Kα), Pb (Lβ), Th (Lα), Rb (Kα), Sr (Kα), Y (Kα), Zr (Kα), and Nb (Kα) analytical lines were excited by the Rh x-ray tube, while Ba (Kα), La (Kα), Ce (Kα), Pr (Kα), and Nd (Kα) lines were analyzed using the Am241 source. Following excitation, overlapping Kα, Kβ, and L-lines were stripped, yielding the "fingerprints" that appear in Figure 2 (cf. Hampel 1984). Background-subtracted net peak intensities were compared and ratioed to the Rh Kα peak continuum (Franzini et al. 1976), then converted to parts per million using a least squares polynomial fit routine (Schamber 1977; Bice 1980:421–422; Hughes 1983a:25–26).

Results

Most of the quantitative trace and rare earth elemental measurements generated from the present non-destructive study (Table 2) are in agreement with those derived from previous destructive analyses (Table 4), and with recommended values for U.S. Geological Survey international rock standards (Table 1). Pr, Cu,

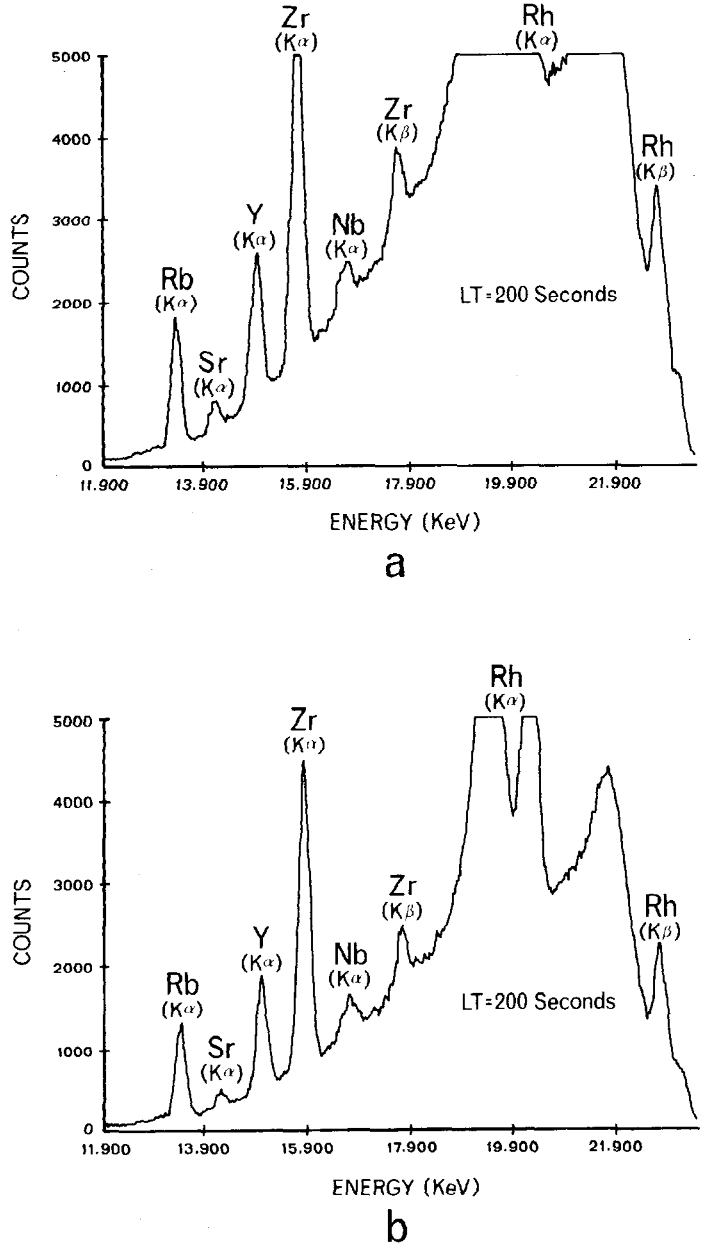

Fig. 2. Energy dispersive x-ray fluorescence "fingerprint" of Obsidian Butte volcanic glass. a) "fingerprint" of pressed powder sample OS-21 (see Table 4); b) "fingerprint" of unmodified obsidian flake sample OB-8 (see Table 2).

and Ni are not measured well by non-destructive x-ray fluorescence, because concentrations for these elements in obsidians often fall below the minimum limits of detection (Vane 1977) at 200 seconds livetime. Computation of coefficients of variation for sample means and standard deviations (Table 3) shows that these measurements vary widely across samples. Th, Nb, and Sr measure-

Table 1. X-ray fluorescence determinations for trace and rare earth element concentrations in three U.S. Geological Survey rock standards compared to recommended values. All values in parts per million. ± = counting error uncertainty (Schamber 1977:249).

U.S. Geological Survey standard	Elements							
	Th	Pb	Nd	Pr	Ce	La	Ba	Nb
W-1 (Flanagan 1976)	2.4	7.8	15.0	3.4	23.0	9.8	160.0	9.5
W-1 (this study)	0.0 ± 0.0	14.0 ± 3.2	15.8 ± 5.4	10.5 ± 5.2	22.8 ± 4.7	12.5 ± 4.1	156.3 ± 7.7	0.0 ± 0.0
GSP-1 (Flanagan 1976)	104.0	51.3	188.0	50.0	394.0	191.0	1300.0	29.9
GSP-1 (this study)	102.5 ± 5.8	52.9 ± 2.8	178.5 ± 11.2	52.8 ± 9.8	393.5 ± 12.5	175.1 ± 9.9	1256.3 ± 22.5	27.8 ± 2.3
G-2 (Flanagan, 1976)	24.2	31.2	60.0	19.0	150.0	96.0	1870.0	13.5
G-2 (this study)	28.2 ± 5.0	33.2 ± 2.6	65.9 ± 9.9	24.0 ± 9.7	149.4 ± 9.1	89.4 ± 8.2	1797.9 ± 28.2	20.9 ± 2.5

U.S. Geological Survey standard	Elements							
	Zr	Y	Sr	Rb	Ga	Zn	Cu	Ni
W-1 (Flanagan 1976)	105.0	25.0	190.0	21.0	16.0	86.0	110.0	76.0
W-1 (this study)	109.0 ± 5.4	22.3 ± 4.5	172.8 ± 6.3	23.8 ± 3.5	14.7 ± 2.8	87.5 ± 6.9	104.5 ± 6.9	69.7 ± 9.2
GSP-1 (Flanagan 1976)	500.0	30.4	233.0	254.0	22.0	98.0	33.3	12.5
GSP-1 (this study)	514.8 ± 5.1	29.4 ± 3.0	238.2 ± 3.9	263.5 ± 4.1	20.4 ± 2.6	95.1 ± 6.8	29.0 ± 2.8	6.8 ± 5.1
G-2 (Flanagan, 1976)	300.0	12.0	479.0	168.0	22.9	85.0	11.7	5.1
G-2 (this study)	309.2 ± 4.9	14.8 ± 3.1	471.5 ± 6.1	170.0 ± 4.0	19.0 ± 2.8	86.1 ± 6.5	5.5 ± 4.9	0.0 ± 0.0

Table 2. Trace element concentration values for 10 source standards from Obsidian Butte. All values in parts per million. ± = counting error uncertainty (Schamber 1977:249).

	Sample designation									
Element	OB-1	OB-2	OB-3	OB-4A	OB-5	OB-8	OB-13A	OB-14	OB-15A	OB-17
Th	11.6	16.9	18.5	20.3	27.3	20.5	15.3	9.6	16.9	22.7
	±4.9	±4.0	±4.2	±3.9	±4.3	±4.6	±4.8	±5.0	±4.4	±4.5
Pb	19.1	20.3	21.9	20.3	18.3	18.8	14.6	16.9	17.6	23.1
	±2.3	±1.9	±1.9	±1.8	±1.9	±2.0	±2.2	±2.4	±2.0	±2.1
Nd	60.3	56.7	60.7	52.1	59.0	59.4	58.6	70.7	49.1	40.4
	±6.4	±6.6	±5.6	±6.2	±7.2	±6.5	±9.8	±8.0	±7.1	±7.4
Pr	14.8	22.9	21.8	0.0	19.5	8.6	17.4	12.8	11.6	6.8
	±5.8	±5.9	±6.8	±0.0	±6.3	±5.7	±8.6	±6.9	±6.1	±6.7
Ce	103.9	125.8	98.4	112.0	121.3	134.8	113.2	125.8	119.0	107.9
	±5.8	±6.3	±6.7	±5.7	±7.0	±6.2	±8.9	±7.3	±6.7	±7.2
La	55.3	50.0	53.0	46.8	44.3	50.1	40.4	57.7	48.8	63.2
	±4.8	±5.1	±5.8	±4.7	±5.6	±5.0	±7.3	±6.0	±5.5	±5.8
Ba	529.4	454.2	550.9	454.1	443.4	439.6	588.5	516.0	452.1	403.2
	±10.8	±10.6	±13.6	±9.9	±11.7	±10.3	±17.4	±13.1	±11.6	±11.9
Nb	17.1	17.7	18.6	22.9	27.3	21.2	20.1	14.4	21.2	27.7
	±2.7	±2.3	±2.4	±2.2	±2.4	±2.6	±2.7	±2.7	±2.5	±2.5
Zr	294.8	277.4	354.0	326.2	313.3	284.1	343.8	256.5	272.6	301.5
	±5.1	±4.1	±4.6	±4.1	±4.3	±4.5	±5.2	±4.9	±4.4	±4.4
Y	87.5	105.8	95.2	112.0	120.2	111.5	87.6	78.5	107.3	124.2
	±4.1	±3.5	±3.5	±3.4	±3.7	±3.9	±4.0	±4.1	±3.8	±3.9
Sr	37.6	26.2	46.1	35.3	24.6	24.0	45.0	32.1	25.5	19.1
	±2.8	±2.1	±2.5	±2.1	±2.2	±2.4	±2.8	±4.8	±2.3	±2.3
Rb	121.4	129.4	123.0	136.2	151.5	135.2	121.0	111.9	123.7	144.0
	±3.8	±3.2	±3.3	±3.1	±3.4	±3.6	±3.7	±3.7	±3.5	±3.5
Ga	19.7	24.1	23.7	28.0	26.6	23.7	20.8	21.1	23.7	20.9
	±2.7	±2.8	±2.9	±2.6	±2.9	±2.7	±2.8	±3.3	±2.6	±2.7
Zn	55.9	57.5	47.2	55.1	58.6	58.2	62.0	50.3	49.8	63.9
	±4.9	±5.0	±4.9	±4.7	±5.2	±4.8	±5.1	±5.8	±4.7	±4.8
Cu	4.0	3.6	5.7	0.0	3.3	5.0	8.4	0.0	7.5	0.0
	±3.6	±3.6	±3.7	±0.0	±3.8	±3.3	±3.9	±0.0	±3.4	±0.0
Ni	0.0	20.7	8.5	0.0	10.3	0.0	0.0	0.0	0.0	0.0
	±0.0	±5.1	±5.2	±0.0	±5.2	±0.0	±0.0	±0.0	±0.0	±0.0

Table 3. Means ($\bar{X}$), standard deviations (S.D.) and coefficients of variation (CV %) for 16 trace and rare earth elements from Obsidian Butte. Means and standard deviations expressed in parts per million; computed from data in Table 2.

Element			Element			Element			Element		
Th	$\bar{X}$	17.96	Pb	$\bar{X}$	19.09	Nd	$\bar{X}$	56.70	Pr	$\bar{X}$	13.63
	S.D.	5.18		S.D.	2.47		S.D.	8.07		S.D.	7.19
	CV %	28.85		CV %	12.92		CV %	14.23		CV %	52.79
Ce	$\bar{X}$	116.21	La	$\bar{X}$	50.96	Ba	$\bar{X}$	483.14	Nb	$\bar{X}$	20.82
	S.D.	11.19		S.D.	6.65		S.D.	59.09		S.D.	4.27
	CV %	9.63		CV %	13.05		CV %	12.23		CV %	20.51
Zr	$\bar{X}$	302.42	Y	$\bar{X}$	102.98	Sr	$\bar{X}$	31.55	Rb	$\bar{X}$	129.73
	S.D.	31.75		S.D.	15.14		S.D.	9.24		S.D.	11.99
	CV %	10.50		CV %	14.70		CV %	29.29		CV %	9.24
Ga	$\bar{X}$	23.23	Zn	$\bar{X}$	55.85	Cu	$\bar{X}$	3.75	Ni	$\bar{X}$	3.95
	S.D.	2.66		S.D.	5.39		S.D.	3.05		S.D.	7.08
	CV %	11.45		CV %	9.65		CV %	81.24		CV %	179.14

Table 4. Trace and rare earth element concentrations for obsidian (OS-21) and whole rock rhyolites from Obsidian Butte. Obsidian Butte and Red Island data from Robinson et al. (1976: table 2); n.m. = not measured; [a] = R. N. Jack, analyst. All values in parts per million.

		Obsidian Butte			Red Island	
Element	OS-21[a]	170-4A	W-772	170-26A	64CMp-107	170-21p
Th	26	n.m.	n.m.	n.m.	n.m.	n.m.
Pb	16	—	—	15	—	10
Nd	62	30	—	70	—	70
Pr	15	n.m.	n.m.	n.m.	n.m.	n.m.
Ce	132	150	—	100	—	150
La	72	70	70	70	30	100
Ba	467	300	700	500	700	500
Nb	31	30	20	20	15	30
Zr	324	300	300	300	300	300
Y	57	100	100	100	100	150
Sr	30	27	50	33	50	25
Rb	144	146	n.m.	137	n.m.	142
Ga	21	30	30	30	50	20
Zn	68	n.m.	n.m.	n.m.	n.m.	n.m.
Cu	6	3	7	7	10	7
Ni	20	n.m.	n.m.	n.m.	—	—
Co	36	—	—	1.5	—	—
Mn	431	n.m.	n.m.	n.m.	n.m.	n.m.
Ti	1074	n.m.	n.m.	n.m.	n.m.	n.m.

ments also are more variable than Pb, Nd, Ce, La, Ba, Zr, Y, Rb, Ga, and Zn, suggesting that they may not be as useful as those remaining elements in distinguishing between obsidian sources (see Hughes 1982:176). However, high "apparent" measurement error (relatively high CV% values) will be registered when the absolute concentration for an element approaches its minimum limits of detection, and when "true" intersource elemental variability exists. In short, it is important to recognize that both instrumental measurement limitations and inherent geochemical variability may be represented in CV% values.

Obsidian Butte trace element concentrations for Ce, Ba, Zr, Y, Sr, and Rb contrast with those for other southern California obsidians (Coso Hot Springs [Jack 1976:table 11.5; Bacon et al. 1981:table 3] Rustler Canyon, San Bernardino can be illustrated using a bivariate scatter diagram (Fig. 5).

In order to test whether the results of the Obsidian Butte analyses could prof-

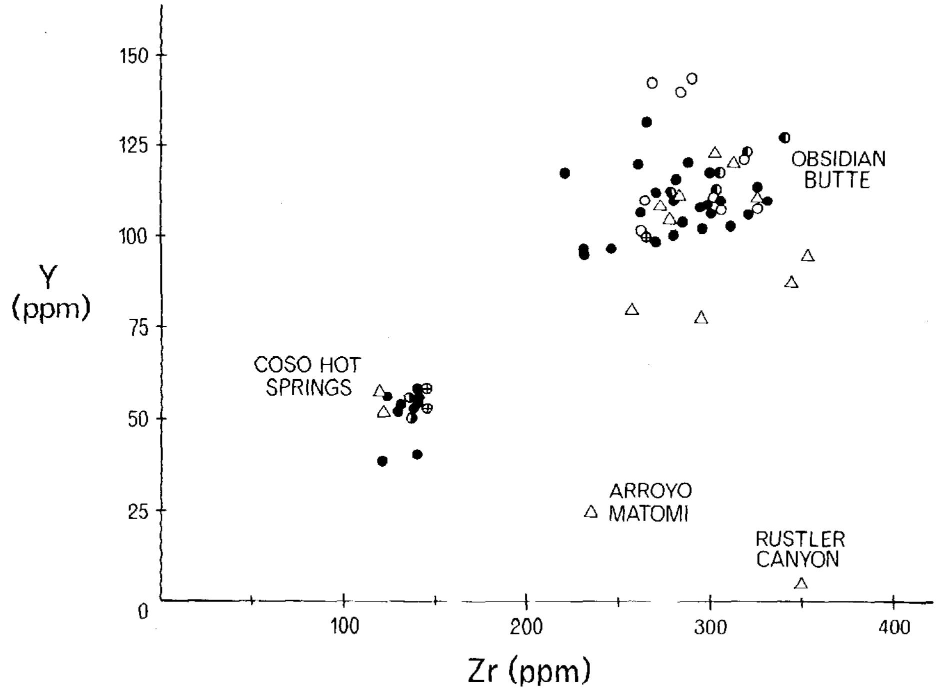

Fig. 3. Scatter diagram of Y vs. Zr concentrations for obsidian source specimens (open triangles) from southern California and Baja California. Circles represent values for artifacts from archaeological sites SDi-682 (●); SDi-813 (O); SDi-5130 (◑); SDi-6071 (◐) and W-1049 (⊕). Obsidian Butte source standards plotted from data in Table 2; Rustler Canyon and Arroyo Matomi (Baja California) values determined by R. N. Jack using wavelength dispersive x-ray fluorescence.

More generally, the agreement between the present analysis and previous destructive work shows that non-destructive analyses can yield concentration estimates (in parts per million) suitable for use in interlaboratory comparisons. The advantages of reporting the results of archaeometric research in standard measurement units (e.g. weight percent or parts per million) have been recognized for some time (see Bieber et al. 1976); the results of the present study indicate that it is now possible to begin building a quantitative geochemical data base for that can readily be used by researchers at other laboratories.

Literature Cited

Bacon, C. R., R. Macdonald, R. L. Smith, and P. A. Baedecker. 1981. Pleistocene high-silica rhyolites of the Coso Volcanic Field, Inyo County, California. J. Geophys. Res., 86(B11):10223–10241.

Bice, D. C. 1980. Tephra stratigraphy and physical aspects of recent volcanism near Managua, Nicaragua. Unpubl. Ph.D. Thesis. Univ. California, Berkeley 422 pp.

Bieber, A. M., Jr., D. W. Brooks, G. Harbottle, and E. V. Sayre. 1976. Application of multivariate techniques to analytical data on Aegean ceramics. Archaeom., 18:59–74.

Ericson, J. E. 1981. Exchange and production systems in Californian prehistory: the results of hydration dating and chemical characterization of obsidian sources. British Archaeol. Repts. Int. Ser. 110.

———, T. A. Hagan, and C. W. Chesterman. 1976. Prehistoric obsidian in California II: geologic and geographic aspects. Pp. 218–239 *in* Advances in obsidian glass studies: archaeological and geochemical perspectives. (R. E. Taylor, ed.), Noyes Press, Park Ridge, New Jersey, viii + 360 pp.

Flanagan, F. J. 1976. 1972 compilation of data on USGS standards. Pp. 131–183 *in* Description and analyses of eight new USGS rock standards. (F. J. Flanagan, ed.), U.S. Geol. Surv. Prof. Pap. 840.

Franzini, L., L. Leoni, and M. Saitta. 1976. Determination of the x-ray mass absorption coefficient by measurement of the intensity of Ag Kα Compton scattered radiation. X-ray Spectrom., 5:84–87.

Friedman, I., and J. Obradovich. 1981. Obsidian hydration dating of volcanic events. Quat. Res., 16:37–47.

Hampel, J. H. 1984. Technical considerations in x-ray fluorescence analysis of obsidian. Pp. 21–25 *in* Obsidian studies in the Great Basin. (R. E. Hughes, ed.), Contrib. Univ. California Archaeol. Res. Facil. 45.

Heizer, R. F., and A. E. Treganza. 1944. Mines and quarries of the Indians of California. Calif. J. Mines and Geol., 40:291–359. (Reprinted 1972 by Ballena Press, Ramona, Calif.)

Hughes, R. E. 1982. Age and exploitation of obsidian from the Medicine Lake Highland, California. J. Archaeol. Sci., 9:173–185.

———. 1983a. Exploring diachronic variability in obsidian procurement patterns in northeast California and southcentral Oregon: geochemical characterization of obsidian sources and projectile points by energy dispersive x-ray fluorescence. Unpubl. Ph.D. Diss., Univ. California, Davis, 422 pp.

———. 1983b. X-ray fluorescence characterization of obsidian. Pp. 401–408 *in* The archaeology of Monitor Valley: 2. Gatecliff Shelter (D. H. Thomas), Amer. Mus. Nat. Hist. Anthrop. Pap., 59:1–552.

———. (ed.). 1984. Obsidian studies in the Great Basin. Contrib. Univ. California Archaeol. Res. Facil. 45.

———, and D. L. True. 1985. Perspectives on the distribution of obsidians in San Diego County, California. North Amer. Archaeol., 6:325–339.

Jack, R. N. 1976. Prehistoric obsidian in California I: geochemical aspects. Pp. 183–217 *in* Advances in obsidian glass studies: archaeological and geochemical perspectives. (R. E. Taylor, ed.), Noyes

Robinson, P. T., W. A. Elders, and L. J. P. Muffler. 1976. Quaternary volcanism in the Salton Sea geothermal field, Imperial Valley, California. Geol. Soc. Amer. Bull., 87:347–360.

Rogers, A. F. 1934. Salton volcanic domes of Imperial County, California. Geol. Soc. Amer. Proc. 1934:328.

Schamber, F. H. 1977. A modification of the linear least-squares fitting method which provides continuum suppression. Pp. 241–257 *in* X-ray fluorescence analysis of environmental samples. (T. G. Dzubay, ed.), Ann Arbor Science Publishers, Ann Arbor, Mich.

Treganza, A. E. 1942. An archaeological reconnaissance of northeastern Baja California and southeastern California. Amer. Antiquity, 8:152–163.

Vane, R. 1977. Trace element sensitivities in geological samples. Nuc. Semicond. Appl. Lab. Rept. CAL-50, United Scientific Corporation, Mountain View, Calif.

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