

Trace Element Geochemistry of Volcanic Glass from the Obsidian Cliffs Flow, Three Sisters Wilderness, Oregon

Abstract

This study was undertaken to investigate potential intrasource trace element variability in the Obsidian Cliffs flow, Three Sisters Wilderness, Oregon. Geologic samples of artifact-quality volcanic glass (obsidians) were collected from twelve locations around the flow, and 80 of these (ten each from eight locations) were subjected to non-destructive energy dispersive x-ray fluorescence analysis. Concentration abundances of eleven minor, trace, and rare earth elements were determined for each collection location. The results show that all locations represent obsidian of the same (Obsidian Cliffs) geochemical type, and they contribute to the long-term goal of establishing a geochemical data base against which artifacts from Oregon archaeological sites can be compared.

Introduction

Until quite recently, obsidian studies have attracted little interest from Oregon archaeologists. Consequently, studies in the state have lagged behind those conducted in California where, for the last two decades, archaeologists have reaped the benefits from the partnership forged with geochemists. There archaeologists have employed volcanic glass studies to investigate (among other topics) differences in prehistoric social ranking, prehistoric trade and exchange, and the production histories of obsidian quarries. Despite this lag, the archaeological potential for Oregon obsidian studies is truly exciting, since the state probably contains as many artifact-quality sources of volcanic glass as arc known from any region of similar size in the world.

However, before the benefits of obsidian studies (in this case, geochemical "fingerprinting" or "sourcing") can be accrued archaeologically, it is first necessary to locate and geochemically characterize parent geologic sources (and source types), since it is to the geochemical "profiles," or "fingerprints," of these volcanic glasses that measurements on archaeological artifacts will be compared. Despite the initial skepticism for obsidian studies that followed disclosure of mistakes in both x-ray analytical techniques and statistical classifications of obsidian sources and artifacts throughout Oregon (Sappington 1981a,b; Toepel and Sappington 1982; see Hughes 1984), subsequent studies (e.g. Hughes 1986a, b; Skinner 1983) have realized some of the potential of such work, and have charted some promising research directions. But before any confidence can be placed in *archaeological* applications of obsidian studies a solid

geochemical foundation must be established, grounded in analyses reported in internationally recognized measurement units calibrated to international rock standards. It is only through adherence to analytically rigorous standards that researchers can begin to build a quantitative data base for Oregon obsidians that can be shared by researchers at different laboratories.

Recognizing this, the ultimate goal of what has come to be called "obsidian sourcing" research should serve two complementary purposes- the first principally *geochemical*, the second principally *archaeological*. First it is necessary to collect and analyze volcanic glasses and to determine whether any geochemical evidence exists for intrasource variability among quarries. Having accomplished the first step, these base-line geochemical data can be employed to investigate archaeological questions regarding the long-term use-life history of obsidian quarries, prehistoric trade and exchange, and mobility patterns. The research reported here was undertaken to investigate only the first of these two issues.

The Problems

The present study is not the first (see Williams [1944] for a geologic description of the flow) to generate trace element data for Obsidian Cliffs volcanic glass but, compared to the geochemical and archaeometric attention devoted to the nearby Newberry Volcano (e.g. Laidley and McKay 1971; Higgins 1973; Friedman 1977; MacLeod and Sherrod 1988), research on the Cliffs is considerably less extensive and detailed. Despite the work conducted to date, three problems remained which required further research. First, geochemical

measurements on obsidian from the Cliffs (Anttonen 1972; S. Hughes 1983; Skinner 1983) remain unpublished and the results have not been widely disseminated. Second, Obsidian Cliffs glass was characterized on the basis of an extremely small number of analyses; Skinner (1983), for example, reported analyses for only five elements on four samples, but it was not altogether clear to what extent these measurements reflected the range of geochemical variability in the source. Third, analyses undertaken to date were essentially *destructive*; that is, some portion of the geologic specimen was crushed and ground into a fine powder prior to wavelength dispersive x-ray fluorescence (WDXRF; see Skinner 1983: Appendix V, p. 6) and neutron activation analysis. While this procedure has a long history in geochemistry, recent advances in computer-based spectrum deconvolution subroutines and automatic matrix-effect correction programs have enabled those employing energy dispersive x-ray fluorescence (EDXRF) on volcanic glasses to conduct *non-destructive* quantitative analyses of both geologic source samples and archaeological artifacts (see Hughes 1986a, b; 1988a, b). Although traditional WDXRF analysis is capable of detecting slightly lower concentrations of certain elements than state-of-the-art energy dispersive instrumentation, this advantage is offset in *archaeological* applications because portions of artifacts are sacrificed (i.e., ground into a powder) prior to WDXRF analysis (Skinner 1983: Appendix IX, p. 12, 17; see also Nelson [1984: 28]). In light of the close comparison between WDXRF, EDXRF and neutron activation measurements on obsidian from the same sources (see Hughes 1984: Table 3; 1986b: Table 4; 1988a: Table II; Hughes and Nelson 1987: Table 1) and archaeology's explicit conservation ethic, it seemed most appropriate to extend the non-destructive method of analysis to Oregon obsidians – specifically, to the Obsidian Cliffs (see also Hughes 1986a).

Field Reconnaissance and Collection

Obsidian source specimens were obtained from 12 outcrops at, and adjacent to, Obsidian Cliffs (see Figures 1 and 2). Observations were made during the field reconnaissance phase regarding the quality of obsidian at each occurrence, variations in glass texture and color and, in particular, evidence for prehistoric utilization at each location. Although some evidence for prehistoric quarrying was ob-

served at all 12 localities, the intensity of such activities (based on qualitative impressions of the amount of quarry-workshop debris on the surface) varied considerably across collection sites. The field collection phase was designed to obtain samples spanning the full range of visual varieties (i.e., colors and texture variations) in the hope that, if macroscopic variation was encoded geochemically, it might be possible to identify subtle intrasource distinctions. Red-and-black mottled obsidian was collected from an *in-situ* occurrence at a prominence along the western margin of the Obsidian Cliffs flow (location 7106, see Figure 1), while mahogany colored varieties were observed and collected at locations 774, 779 and 789 and 7148. Despite a previously reported occurrence of red obsidian at Obsidian Cliffs (C. Skinner, pers. comm.), the prevailing convention among local archaeologists has been that glass of red or red-and-black physical appearance must have been conveyed from sources to the east of the Cascades (e.g. Glass Buttes) where red obsidians are well-known (C. Davis, pers. comm.).

The choice of particular site collections for subsequent geochemical analysis was influenced by the preceding factors and by the areal extent and abundance of observed quarry-workshop debris. Lacking any clear understanding of the production history of the Obsidian Cliffs quarries (i.e., how long they were used, what kinds of prehistoric manufacturing activities were undertaken at each, whether or not their use-life histories had changed through time), it seemed advisable to focus initial research efforts on the quarries (sites) which had the greatest surface densities of artifact manufacturing debris on the assumption that such densities could serve as general indicators of the importance of each source in the past. Consequently, of the twelve collecting locations, samples from eight (nos. 774, 775, 777, 778, 782, 7106, 7138, and 7148 on Figure 2) were later subjected to x-ray fluorescence analysis.

Laboratory Analysis: Methods

Laboratory investigations were performed on a Spectrace™ 5000 (Tracor X-ray) energy dispersive x-ray fluorescence spectrometer equipped with a rhodium (Rh) x-ray tube, a 50 kV x-ray generator, and a Si(Li) solid state detector with 150 eV resolution (FWHM) at 5.9 keV in a 30 mm² area. The x-ray tube was operated at 30.0 kV, 0.30 mA,



Figure 1. Aerial view to southeast across the Obsidian Cliffs flow (lower left in photo), with Collier Cone and the North Sister in background. Arrow specifies the terminus of the flow, which corresponds with collection location 7106 on Figure 2.

using a 0.127 mm Rh primary beam filter in an air path at 200 seconds livetime to generate x-ray intensity data for elements Zn ($K\alpha$), Ga ($K\alpha$), Rb ($K\alpha$), Sr ($K\alpha$), Y ($K\alpha$), Zr ($K\alpha$), and Nb ($K\alpha$). Ti ($K\alpha$), Mn ($K\alpha$), and total iron ($Fe_2O_3^T$) intensities were generated by operating the x-ray tube at 15.0 kV, 0.30 mA, with a 0.127 mm aluminum (Al) filter in an air path at 200 seconds livetime, while Ba ($K\alpha$) intensities were generated by operating the x-ray tube at 50.0 kV, 0.35 mA, with a 0.63 mm copper (Cu) filter at 300 seconds livetime. Trace

element intensities were converted to concentration estimates by employing a least-squares calibration line established for each element from analysis of up to 25 international rock standards certified by the U.S. Geological Survey, the U.S. National Institute of Standards and Technology, the Geological Survey of Japan, and the Centre de Recherches Petrographiques et Geochimiques (France). Further details pertaining to x-ray tube operating conditions, calibration and element-specific detection limits appear in Hughes (1988a). The x-ray analyses were

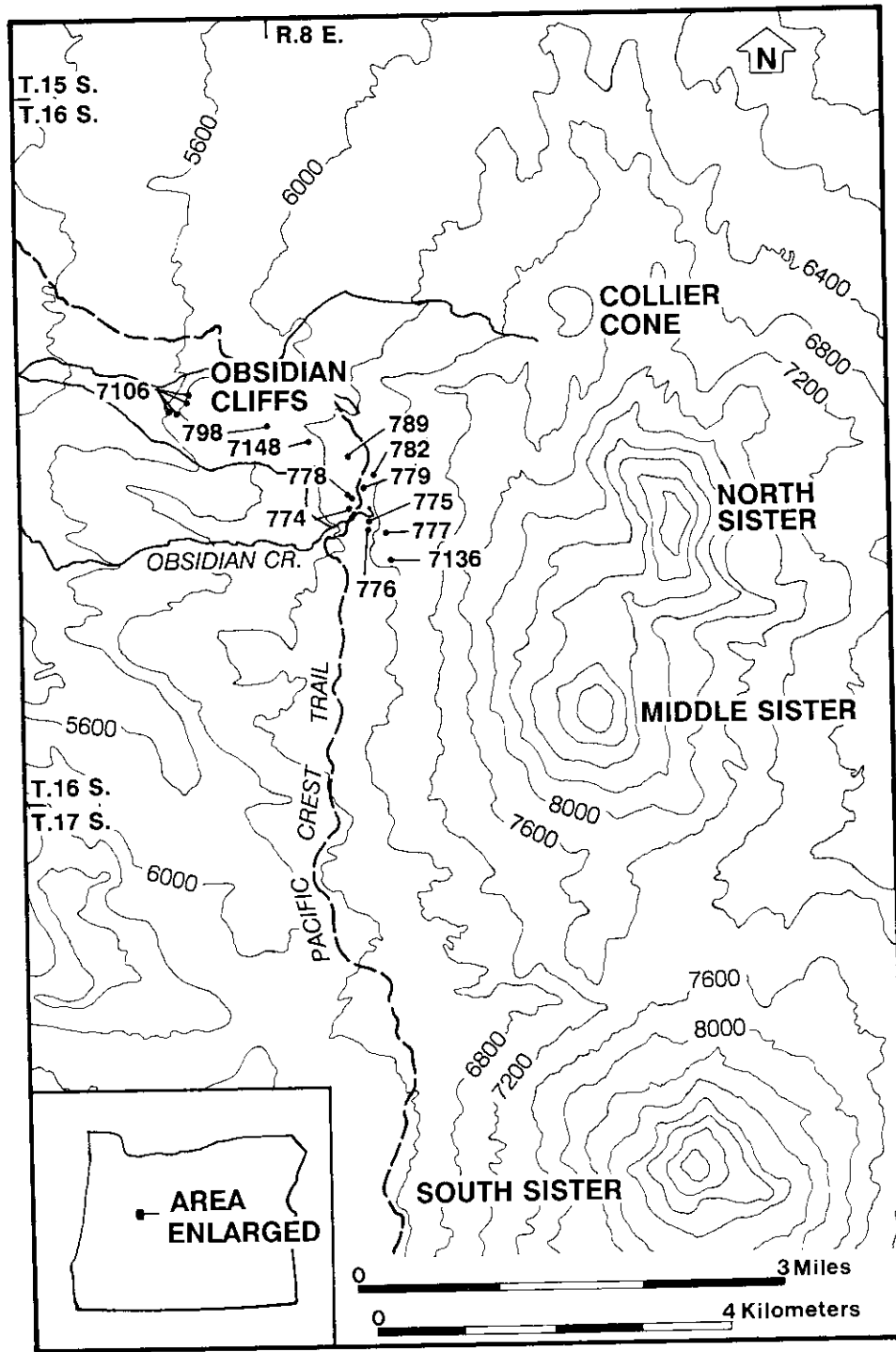


Figure 2. The state of Oregon (inset) showing the location of the study area in the Cascade Range. Numbers around Obsidian Cliffs refer to the sites from which geologic samples were collected (see Table 1).

TABLE 1. Trace, rare earth and selected minor element contents of volcanic glass collected from eight areas at Obsidian Cliffs (see Figure 2 for locations). All elemental values in parts per million, except iron (Fe), expressed as total iron ($\text{Fe}_2\text{O}_3^{\text{T}}$) in weight percent. \bar{X} = sample mean; S.D. = sample standard deviation; CV% = coefficient of variation. Ten specimens analyzed from each site. Site numbers assigned by Willamette National Forest personnel.

Element		Collection Locations							
		774	775	777	778	782	7106	7136	7148
Ti	\bar{X}	597	604	596	616	586	627	615	612
	S.D.	37	31	22	52	37	24	36	53
	CV%	6	5	4	8	6	4	6	9
Mn	\bar{X}	384	383	381	378	382	378	384	390
	S.D.	12	9	8	5	10	7	9	7
	CV%	3	2	2	1	3	2	2	2
$\text{Fe}_2\text{O}_3^{\text{T}}$	\bar{X}	1.20	1.22	1.22	1.20	1.21	1.19	1.21	1.24
	S.D.	.03	.03	.03	.02	.03	.01	.03	.06
	CV%	2	2	2	1	3	1	2	4
Zn	\bar{X}	45	43	45	43	41	42	45	46
	S.D.	6	5	5	3	6	4	7	5
	CV%	13	11	11	6	13	10	14	11
Ca	\bar{X}	16	16	17	18	18	18	17	16
	S.D.	2	3	2	1	2	1	3	3
	CV%	11	17	11	6	12	8	18	16
Rb	\bar{X}	76	76	78	76	75	78	77	75
	S.D.	2	3	3	2	3	2	3	2
	CV%	3	3	4	2	3	2	3	3
Sr	\bar{X}	101	102	102	103	102	102	102	106
	S.D.	4	3	2	4	5	3	4	6
	CV%	4	3	2	4	5	3	4	6
Y	\bar{X}	18	18	18	18	18	17	17	18
	S.D.	1	1	1	1	1	1	1	1
	CV%	4	4	7	6	6	7	6	8
Zr	\bar{X}	88	85	88	87	86	88	89	92
	S.D.	2	2	3	3	5	5	3	5
	CV%	3	2	3	3	5	6	3	5
Nb	\bar{X}	7	8	8	8	8	9	9	8
	S.D.	2	2	2	2	3	2	3	3
	CV%	26	23	28	23	33	23	30	32
Ba	\bar{X}	877	845	899	821	866	824	851	897
	S.D.	33	23	34	20	21	36	45	29
	CV%	4	3	4	3	3	4	5	3

completely non-destructive; cortex-free obsidian flakes and chunks were detached from geologic samples and each was rinsed in distilled water to remove any possible surface contaminants.

Laboratory Analysis: Results

Trace element values generated for 80 samples from eight sampling locations appear in Table 1.

Examination of sample means and standard deviations reveals that all eight sites contain obsidian of remarkably uniform geochemical composition; in fact, mean values for all eight of the best measured elements overlap at two sigma. Thus, there is sound justification for concluding that these eight locations represent exposures of obsidian of the same geochemical type. The values in Table 1 also

are in very close agreement with those generated on a small number of Obsidian Cliffs samples by Skinner (1983: Appendix X), illustrating that non-destructive quantitative EDXRF provides concentration estimates congruent with those generated using the destructive WDXRF technique.

The present study greatly expands the number of minor, trace and rare earth element measurements for Obsidian Cliffs glass (from five in Skinner's study to eleven in Table 1 herein), and these additional elements will likely be of assistance in helping to distinguish between Obsidian Cliffs glass and other obsidians which have similar Rb, Sr, and Zr compositions (e.g. Inman Creek Gravels, Group B; Skinner 1983). The trace element data in Table 1 are quite different from artifact-quality obsidians from the nearby Newberry Volcano (see Table 2; cf. MacLeod and Sherrod [1988: Table 1]) and with the porphyritic microvesicular obsidians of the South Sister in the Cascade Range (Macdonald et al 1992: Appendix 1, [specimens 8-10], p.170). The geochemical contrasts among sources are illustrated in Figure 3 using a bivariate plot of Zr vs. Sr abundance.

Discussion

Although quantitative measurements (values reported in parts per million [ppm] and weight percent [%] composition) are reported here for eleven minor, trace and rare earth elements, not all elements are equally useful in obsidian characterization studies. The best elements to employ for inter-source discrimination are those I term "diagnostic" (see also Hughes 1990)- those minor, trace, and/or rare earth elements that are well-measured by x-ray fluorescence, and whose concentrations show low variability *within* a source and marked variability *across* sources. Diagnostic elements are those whose concentration values allow one to draw the clearest geochemical distinctions between sources. In practice, the actual identification of a diagnostic element and suites of diagnostic elements is influenced not only by instrument sensitivity and analytical technique (e.g., x-ray fluorescence vs. neutron activation), but by the concentration of a particular element in a source under study.

TABLE 2. Trace element geochemistry of seven obsidians in the vicinity of the Newberry Volcano, Oregon. All values in parts per million (ppm), except iron (Fe) expressed as Fe_2O_3 in weight percent; \bar{X} = sample mean, S.D. = sample standard deviation, CV% = coefficient of variation (in percent). Five specimens were analyzed from each source, except McKay Butte (n=3).

Element		Big Obsidian Flow (188-)	Game Hut (189-)	Pumice Cone (191-)	North Flow (190-)	East Lake (192-)	McKay Butte	Quartz Mtn.
Ti	\bar{X}	1350	1385	1416	1358	1475	1165	568
	S.D.	52	55	66	65	70	48	31
	CV%	4	4	5	5	5	4	6
Mn	\bar{X}	589	455	466	447	466	387	376
	S.D.	12	18	11	24	12	3	4
	CV%	2	4	2	5	3	1	1
Fe_2O_3 ^T	\bar{X}	2.60	2.25	2.29	2.23	2.36	1.97	1.84
	S.D.	.05	.06	.05	.09	.05	.04	.03
	CV%	2	3	2	4	2	2	2
Rb	\bar{X}	117	127	126	129	126	125	130
	S.D.	1	6	3	7	4	5	5
	CV%	1	5	3	6	4	4	4
Sr	\bar{X}	53	60	59	59	62	59	61
	S.D.	2	3	4	3	3	2	2
	CV%	4	5	6	5	4	3	3
Y	\bar{X}	42	38	39	37	36	35	38
	S.D.	1	3	3	3	2	1	2
	CV%	3	8	6	7	6	4	5
Zr	\bar{X}	349	277	275	274	275	195	178
	S.D.	3	7	7	6	8	8	4
	CV%	1	3	2	2	3	4	2

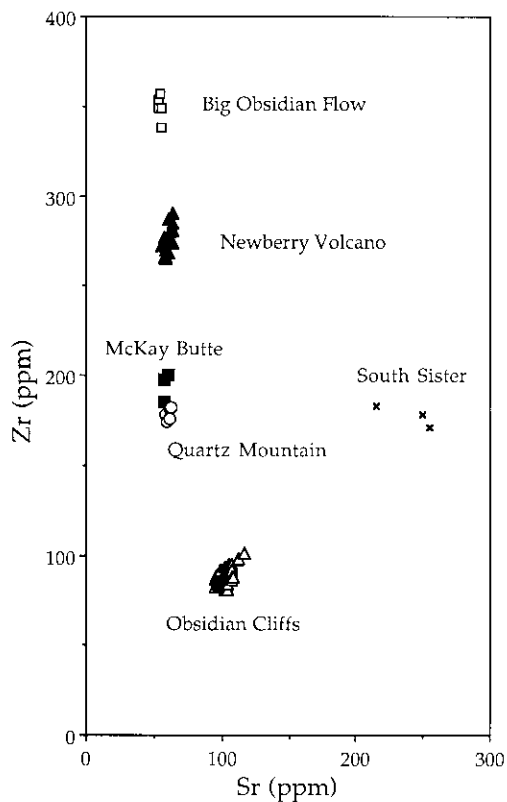


Figure 3. Bivariate plot of Zr vs. Sr abundances in five major Cascade Range obsidian source (chemical) types. Plots made from raw data summarized in Tables 2 and 3 herein, except South Sister (data from Macdonald et al. 1992: Appendix I, p. 128, specimens 8-10). Open squares represent obsidian from the Big Obsidian Flow; Newberry Volcano; filled triangles represent four source localities (Game Hut, Pumice Cone, North, and East Lake flows) in the Newberry Volcano; filled squares represent McKay Butte; open circles Quartz Mountain; and open triangles depict Obsidian Cliffs obsidian. South Sister porphyritic microvesicular obsidian is represented on the diagram by x symbols.

For example, Sr is in most cases an extremely useful trace element in obsidian sourcing studies because it can be measured with good precision using x-ray fluorescence analysis and its concentrations vary by several orders of magnitude across sources (Jack and Carmichael 1969: 22; Macdonald et al. 1992: 103). Occasionally, however, Sr content may not be diagnostic for glasses containing \leq ca. 10-15 ppm because such concentrations are near the calibration-imposed detection limits of x-ray fluorescence instrumentation (e.g., Dog Hill obsidian [Hughes 1986a: Table 2]). In

the Obsidian Cliffs case, Sr is a diagnostic element since it occurs in concentrations considerably above detection limits, it varies markedly across sources, and coefficients of variation (see Hughes 1984) for all Obsidian Cliffs collection sites show that it is measured with precision. On the basis of measurement precision (as monitored by CV% values; Table 1), Ti, Mn, $Fe_2O_3^T$, Rb, Y, Zr and Ba also could be considered diagnostic elements. Zn, Ga and Nb ppm concentrations also were measured and reported for each collection location, but these elements are not considered diagnostic because they do not usually vary significantly across obsidian sources (see Hughes 1982, 1984, 1986b), and because coefficients of variation for these three elements are much larger than those of the remaining eight. Although Zn, Ga and Nb were not diagnostic elements in this particular study, each element has to be evaluated on a case-by-case basis since it is clear that volcanic glasses occur in which some of these (e.g., Nb in certain Idaho [Nelson 1984: Table 5, source #38], Arizona [Jack 1971: Table 1] and New Mexico [Hughes 1988b] obsidians) and other elements (e.g., Sn in certain Peruvian obsidian [Macdonald et al. 1992: Appendix I, specimen 160]) can serve in a diagnostic capacity.

Conclusions

There are several points that should be made with regard to these geochemical findings. To the extent that this uniform minor, trace and rare earth element profile monitors underlying geochemical homogeneity, it should now be possible to pursue obsidian hydration studies to address questions relating to the use-life history of the Obsidian Cliffs source since the probability of intrasource heterogeneity of sufficient magnitude to affect obsidian hydration rate development now appears exceedingly slight. Major and minor element composition data to support this conclusion appear in Skinner (1983: Appendix VII, Table VII-1). Likewise, the geochemical uniformity across all toolstone-caliber varieties of Obsidian Cliffs volcanic glass suggests, as has been documented elsewhere in North America (Griffin et al. 1969; Jackson 1974; Hughes 1986b), that color of obsidian (i.e. red vs. black) carries little significance in provenance studies. The present study underscores again that there is no geochemical justification for the presumption that, in Willamette Valley sites, for example, red obsidian must have been procured

from sources to the east of the Cascades since it couldn't be obtained "locally" (i.e., at Obsidian Cliffs or in its derived river gravels).

Finally, beyond their immediate geochemical utility of contributing to the establishment of a comprehensive multi-element regional data base for Oregon obsidians to which archaeological artifacts can be compared, these geochemical data promise to be pivotal in subsequent archaeological studies; in particular those concerned with reconstructing synchronic and diachronic aspects of prehistoric procurement and conveyance systems (trade and exchange), studies focusing on change and stability in prehistoric settlement subsistence systems and population mobility, and research directed toward identifying functional and temporal variability in the obsidian tool production history of the Obsidian Cliffs.

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