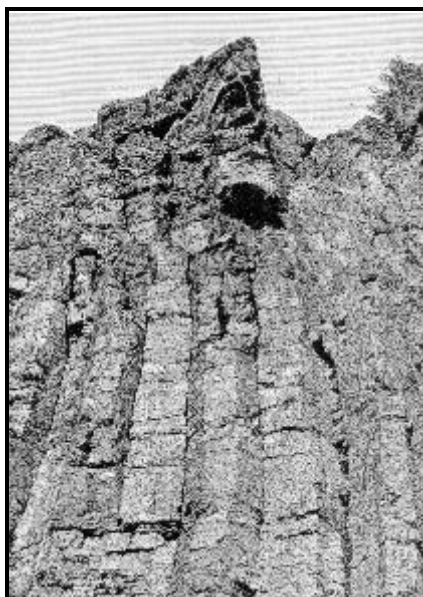


**X-Ray Fluorescence Analysis of an Obsidian Biface from
the Fort Hill Site, Highland County, Ohio**



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Northwest Research Obsidian Studies Laboratory Report 96-48

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Introduction

A single obsidian biface fragment from the Fort Hill Site, Highland County, Ohio, was submitted for X-ray fluorescence trace element provenience analysis. The sample was prepared and analyzed at the Northwest Research Obsidian Studies Laboratory under the accession number BO-96-48.

Analytical Methods

X-ray Fluorescence Analysis and Characterization Studies

Introduction. Although a variety of physical, optical, petrographic, and chemical attributes are used to characterize volcanic glasses, the use of trace element abundances to "fingerprint" obsidian sources and artifacts has shown the greatest overall success. X-ray fluorescence analytical methods, with their ability to nondestructively and accurately measure trace element concentrations in obsidian, have been widely adopted for this purpose (Harbottle 1982; Rapp 1985).

Most geologic sources of obsidian are quite homogeneous in their trace element composition, yet demonstrate adequate intersource variability so that individual sources of glass can be distinguished. Because obsidian can be widely dispersed from its primary geologic source due to a variety of geologic and geomorphic processes, specimens of chemically identical glass are sometimes recovered from outcrops spread over large geographic areas (Hughes 1986a; Hughes and Smith 1993; Skinner 1983:52–56). These secondary source boundaries are often not as well documented as primary sources but must be carefully considered in obsidian procurement studies. Hughes (1986a) points out that these chemically identical obsidian outcrops must be considered as a single chemical group or chemical type and his terminology is followed here.

From small scale (household and site) to large scale (regional and interregional) levels of analysis, the spatial source patterning of characterized obsidian artifacts is influenced by many different environmental and cultural factors. Interpretation of these patterns can provide valuable information about the prehistoric behavioral and environmental procurement variables responsible for observed artifact distributions. At the site level of analysis, patterns of source use may suggest the presence of specific activity areas, of single tool manufacturing events, or, in special cases, may point to differential access of goods and the existence of non-egalitarian social structures. At the intersite or regional level of investigation, the geographic patterning of artifacts can provide information about seasonal procurement ranges, territorial and ethnic boundaries, the location of trails and travel routes, the curatorial value of particular sources or formal artifact types, cultural preferences regarding glass quality and colors, the presence of trade and exchange systems, the existence of intergroup interaction, and the exchange of prestige items between elites of different groups (Ericson 1981; Hughes 1978, 1990; Hughes and Bettinger 1984; Skinner 1983:87–91, 1995a:4.10). The effects of environmental influences such as the distance to source, the location of alternative or competing sources of lithic materials, the

distribution of raw materials in secondary deposits, or the presence of potential barriers such as mountain ranges, must all be considered. Bias introduced during sampling by certain recovery methods, artifact size, and the use of small numbers of samples may also effect the reconstruction of the spatial patterning of analyzed artifacts.

Sample Preparation Methods. Obsidian samples selected for X-ray fluorescence analysis are typically restricted to clean artifacts (a wash with tap water and a brush will usually suffice) with a relatively flat surface at least 10 mm in diameter and at least 1.5 mm thick. Although it is possible to analyze slightly smaller samples (7-10 mm in diameter and 0.5-1.0 mm thick), these items will show some distortion in trace element values and may not be able to be reliably characterized. This is particularly true in areas with complex source use patterns. Source assignments of samples that do not meet the minimum reliable size criteria of 10 mm diameter and 1.5 mm thickness, and/or show distorted trace element values are indicated by an asterisk in the data tables that appear in the appendices.

Analytical Methods. Analysis of the samples were completed using a Spectrace 5000 energy dispersive X-ray fluorescence spectrometer. The system is equipped with a Si(Li) detector with a resolution of 155 eV FWHM for 5.9 keV X-rays (at 1000 counts per second) in an area 30mm². Signals from the spectrometer are amplified and filtered by a time variant pulse processor and sent to a 100 MHz Wilkinson type analog-to-digital converter. The X-ray tube employed is a Bremsstrahlung type, with a rhodium target, and 5 mil Be window. The tube is driven by a 50 kV 1 mA high voltage power supply, providing a voltage range of 4 to 50 kV. The principles of X-ray fluorescence analytical methods are reviewed in detail by Norrish and Chappel (1967), Potts and Webb (1992), and Williams (1987).

For analysis of the elements zinc (Zn), lead (Pb), thorium (Th), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), and niobium (Nb), the X-ray tube is operated at 30 kV, 0.45 mA (pulsed), with a 0.127 mm Pd filter. Analytical lines used are Zn (K-alpha), Pb (L-alpha), Th (L-alpha), Rb (K-alpha), Sr (K-alpha), Y (K-alpha), Zr (K-alpha) and Nb (K-alpha). Samples are scanned for 200 seconds live-time in an air path.

Peak intensities for the above elements are calculated as ratios to the Compton scatter peak of rhodium, and converted to parts-per-million (ppm) by weight using linear regressions derived from the analysis of twenty rock standards from the U.S. Geological Survey, the Geologic Survey of Japan, and the National Bureau of Standards. The analyte to Compton scatter peak ratio is employed to correct for variation in sample size, surface irregularities, and variation in the sample matrix.

For analysis of the elements titanium (Ti), manganese (Mn), and iron (Fe₂O₃^T), the X-ray tube is operated at 12 kV, 0.27 mA with a 0.127 mm aluminum filter. Samples are scanned for 200 seconds live-time in a vacuum path. Analytical lines used are Ti (K-alpha), Mn (K-alpha), and Fe (K-alpha).

Concentration values (parts per million for titanium and manganese, weight percent for iron) are calculated using linear regressions derived from the analysis of thirteen standards from the U.S.

Geological Survey, the Geologic Survey of Japan and the National Bureau of Standards. However, these values are *not* corrected against the Compton scatter peak or other scatter region, and we recommend against using them for anything other than approximate concentrations. Iron/titanium (Fe/Ti) and iron/manganese (Fe/Mn) peak ratios are supplied for use as corrected values.

A word of caution about titanium, manganese and iron concentration values (i.e., titanium ppm, manganese ppm, and iron weight percent)—as mentioned above, these values are not corrected against the Compton Scatter peak or other scatter region, resulting in lower than normal trace element values for small samples that fall below the minimum size requirement. The absence of a spectral reference also means that these values are subject to matrix effects errors. To compensate for these effects, iron-manganese and iron-titanium peak ratios are provided for use as corrected values. To ensure comparability among samples of different sizes, source assignments in all reports are based upon these ratios, and not on the absolute concentration values.

All samples are scanned as unmodified rock specimens. Reported errors represent counting and fitting error uncertainty only, and do not account for instrumental precision or effects related to the analysis of unmodified obsidian. When the latter effects are considered, relative analytical uncertainty is estimated to be between three and five percent.

In traditional X-ray fluorescence trace element studies, samples are powdered and pelletized before analysis (Norrish and Chappel 1967; Potts and Webb 1992). In theory, the irregular surfaces of most obsidian artifacts should induce measurement problems related to shifts in artifact-to-detector reflection geometry (Hughes 1986a:35). Early experiments with intact obsidian flakes by Robert N. Jack, and later by Richard Hughes, however, indicate that analytical results from lenticular or biconvex obsidian surfaces are comparable to those from flat surfaces and pressed powder pellets, paving the way for the nondestructive analysis characterization of glass artifacts (Hughes 1986a:35–37; Jack 1976). The minimum optimal sample size for analysis has been found to be approximately 10 mm in diameter and 1.5–2.0 mm thick. Later experimental studies conducted by Shackley and Hampel (1993) using samples with flat and slightly irregular surface geometries have corroborated Hughes' initial observations. In a similar experiment, Jackson and Hampel (1993) determined that for accurate results the minimum size of an artifact should be about 10 mm in diameter and 1.5 mm thick. Agreement between the U. S. Geological Survey standard RGM-1 (Glass Mountain obsidian) values and obsidian test samples was good at 1 mm thickness and improved markedly to a thickness of 3 mm.

Correlation of Artifacts and Geologic Sources. Trace element values used to characterize the samples are compared directly to those for known obsidian sources such as those reported by Davis et al. (1995), Erlandson et al. (1992), Hamusek (1993, 1995), Hughes (1986a, 1986b, 1988, 1993, 1994), Hughes and Nelson (1987), Jack (1976), Jackson (1986, 1989), Nelson (1984), Nelson and Holmes (1979), Shackley (1991, 1992, 1995), Skinner (1983, 1986), and with unpublished trace element data collected by Northwest Research through analysis of geologic source samples. Artifacts are correlated to a parent obsidian source or chemical source group if diagnostic trace element values fall within about two standard deviations of the analytical

uncertainty of the known upper and lower limits of chemical variability recorded for the source. Occasionally, visual attributes are used to corroborate the source assignments although sources are never assigned on the basis of only megascopic characteristics.

Diagnostic trace elements, as the term is used here, refer to trace element abundances that show low intrasource variation and uncertainty along with distinguishable intersource variability. In addition, this refers to elements measured by X-ray fluorescence analysis with high precision and low analytical uncertainty. In short, diagnostic elements are those that allow the clearest geochemical distinction between sources. Trace elements generally refer to those elements that occur in abundances of less than about 1000 ppm in a sample. For simplicity in this report, we use the term synonymously with major and minor elements such as iron, titanium, and manganese, which may be present in somewhat larger quantities.

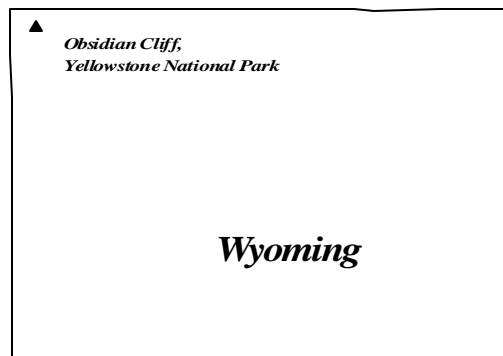
Results of Analysis

X-Ray Fluorescence Analysis

The trace element values for the obsidian biface correspond very well with those of Obsidian Cliff, Yellowstone National Park, Wyoming (Figures 1 and 3). Analytical results are presented in Table A-1 in the Appendix and are summarized in Figure 2.

The spectacular Obsidian Cliff source was one of the first obsidian sources to be described in modern scientific literature (Holmes 1879; Iddings 1888). Artifacts from many sites in North Dakota, South Dakota, Iowa, Illinois, Ohio, Wisconsin, Michigan, Montana, Wyoming, and central Canada have yielded generally small numbers of artifacts correlated with this Yellowstone source (Anderson et al. 1986; Brose 1994; Davis et al. 1995; Griffin et al. 1969; Hatch 1990; Hughes and Nelson 1987; Stewart 1994; Vehik and Baugh 1994). The geology, geochemistry, and prehistoric use of obsidian from Obsidian Cliff are best summarized and described by Davis et al. (1995).

Figure 1. Location of Obsidian Cliff, Yellowstone National Park.



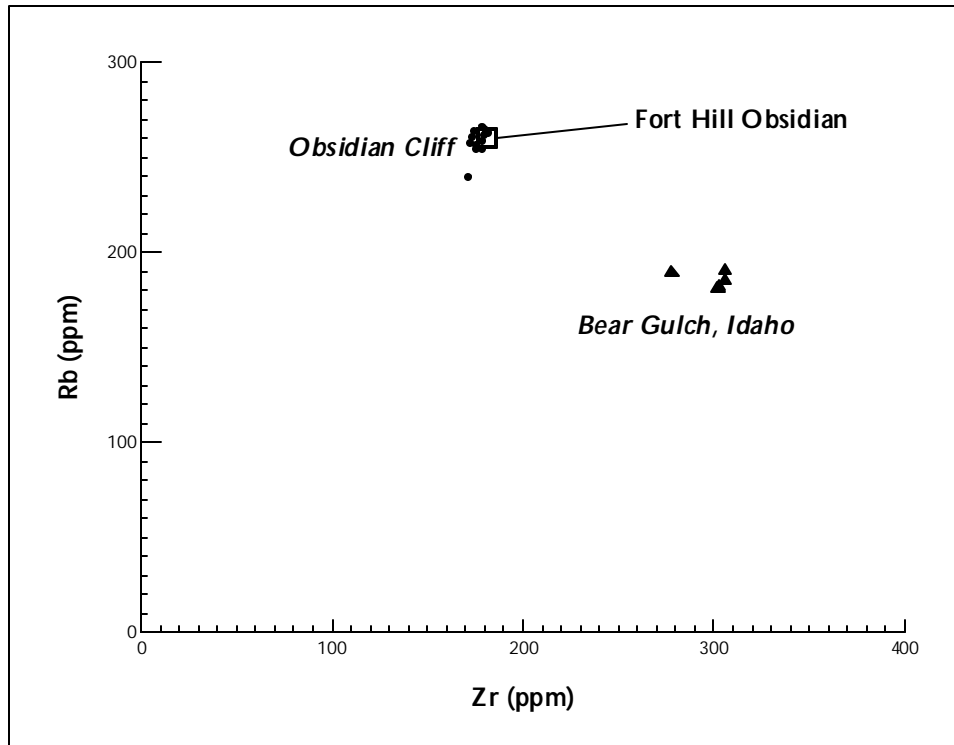


Figure 2. Scatterplot of rubidium (Rb) plotted versus zirconium (Zr) for the Fort Hill artifact and major Hopewell obsidian sources.

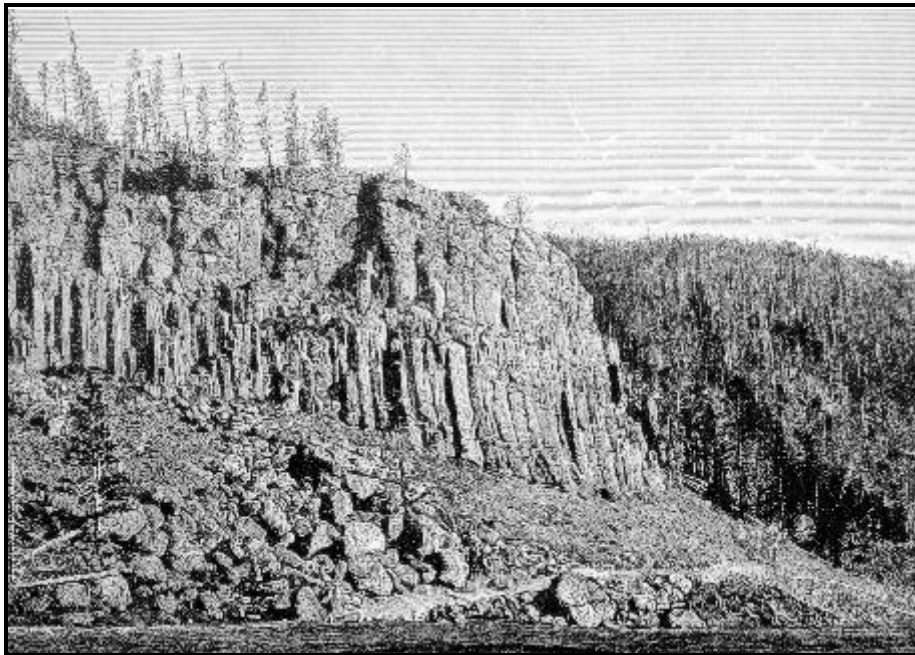


Figure 3. Obsidian Cliff, Yellowstone National Park, Wyoming (Iddings 1988). The obsidian column pictured on the front cover of the report is also from Iddings.

The biface analyzed in the current investigation was recovered from the Fort Hill Site, Ohio, and is mentioned by Griffin (1965) in his discussion of obsidian in the Hopewell sites of the Midwest. The presence of obsidian and other exotic stone, mineral, and marine products is often used to characterize the Middle Woodland cultures collectively known as the Hopewell Culture. The volume and diversity of these exotic materials led to the postulation of a wide-ranging Hopewell Interaction Sphere that was thought to link the Hopewell centers throughout the Midwest by an organized and structured system of trade and exchange (Struever and Houart 1972; Seaman 1979). Although the existence of formalized Hopewell exchange networks has been questioned in more recent years in the light of competing long-distance direct procurement and down-the-line exchange models, there is no doubt that the obsidian found in Hopewell sites was transported long distances from its original source (Stewart 1994).

The obsidian sources of Yellowstone National Park, Wyoming, were long thought to have provided the obsidian found in Hopewell sites (Griffin 1965). Trace element studies of Hopewell obsidian artifacts eventually confirmed Obsidian Cliff in Yellowstone National Park as the major primary source of most Hopewell obsidian artifacts (Griffin et al. 1969; Davis et al. 1995). A second major source of obsidian, the Bear Gulch source, originally thought to have also been located in Yellowstone National Park, was later identified in the Camas-Dry Creek area of eastern Idaho (Hughes and Nelson 1987; Wright et al. 1990).

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Appendix

Results of X-Ray Fluorescence Analysis

Northwest Research Obsidian Studies Laboratory

Table A-1. Results of XRF Studies: Fort Hill Site, Highland County, Ohio

Site	Spec. No.	Catalog No.	Trace Element Concentrations											Ratios		Artifact Source/Chemical Type
			Zn	Pb	Rb	Sr	Y	Zr	Nb	Ti	Mn	Ba	Fe ₂ O ₃ ^T	Fe:Mn	Fe:Ti	
33-HI-1	1	2189/212	78	41	260	4	81	181	47	440	190	NM	1.27	76.9	91.8	Obsidian Cliff, WY
			± 7	4	4	9	3	8	2	95	47	NM	0.11			
NA	RGM-1	RGM-1	37	24	152	107	24	217	11	1669	291	NM	1.99	69.5	38.2	RGM-1 Reference Standard
			± 7	4	3	9	3	8	1	97	47	NM	0.11			

All trace element values reported in parts per million; ± = analytical uncertainty estimate (in ppm). Iron content reported as weight percent oxide.
 NA = Not available; ND = Not detected; NM = Not measured.; * = Small sample.