Trace Element and Visual Characterization Studies of Obsidian from Sites 35-PO-15 and 35-PO-47, Willamette Valley, Western Oregon: An Archaeological Application of Atomic Absorption Spectrometry

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Introduction

Although a variety of different physical, optical, petrographic, and geochemical characteristics have been used to characterize obsidian glasses, the use of trace element abundances to "fingerprint" obsidian sources and artifacts has shown the greatest overall success. In recent years, 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; Williams-Thorpe 1995). The patterns of obsidian source procurement and use revealed by the characteristic trace element signatures of characterized obsidian artifacts can provide unique information about prehistoric behavior. In obsidian hydration dating studies, the chemical composition of obsidian is also a key variable affecting the rate of hydration. It is critical to be able to distinguish among the different geochemical sources encountered during obsidian hydration investigations.

The analytical hardware used for X-ray fluorescence studies, however, is relatively expensive to purchase and maintain and is not readily available in many research settings. As a result, most X-ray fluorescence investigations of artifacts are channeled through a limited number of private contractors or university laboratories, often an expensive and time-consuming process. In this paper, we investigate the utility of an additional analytical method that can be used for the trace element characterization of obsidian artifacts, atomic absorption spectrometry (AAS). This technique offers several different characteristics that make it attractive as an alternative obsidian characterization method:

1. AAS is an analytical technique that is widely available in many academic and commercial settings and is equally or more widely accessible (and affordable) than many other analytical methods used for trace element analysis.
2. The analytical hardware required for AAS analysis costs only a fraction of that needed for X-ray fluorescence analysis.
3. AAS methods are suitable for the accurate and reliable determination of

many of the same trace elements that have been proven to be useful in the characterization of obsidian, e.g., rubidium (Rb), strontium (Sr), zirconium (Zr), and barium (Ba).

We chose to test the method using a small collection of obsidian flakes recovered from two central Willamette Valley archaeological sites, 35-PO-15 and 35-PO-47. At the same time, geologic obsidian samples from the three major geochemical obsidian source groups previously identified in Willamette Valley obsidian characterization studies, Inman Creek A, Inman Creek B, and Obsidian Cliffs, were also analyzed (Skinner n.d.).

The Sites: 35-PO-15 and 35-PO-47

Test excavations were undertaken in the summer of 1990 at two sites, 35-PO-15 (Sec. 28, T9S, R4W) and 35-PO-47 (Sec. 33, T9S, R4W) located in the Luckiamute Valley, a tributary of the Willamette River, Polk County, Oregon (see figures 1 and 2). A radiocarbon date of 4800 ± 80 years ago (uncorrected) is associated with 35-PO-15, and artifacts from the site agree with that Middle Archaic date. Radiocarbon dates were not ascertained for 35-PO-47, nor were temporally sensitive artifacts recovered during excavations. Prior surface collections, however, suggest that the site dates to the Late Archaic Period Fuller Phase (AD 200-1750). The results of the test excavations have also been previously described by Baxter and Smith (1994).

The field methods consisted of placing a line of 1x1 m test pits along the bank of the river, along the edge of a modern agricultural field. Ten centimeter arbitrary excavation levels were removed to culturally sterile soil. It was clear that the sites extend back from the river into the fields, but excavation was not allowed in that area.

Excavations revealed very similar site assemblages, and given their river side locations it seems likely that the two sites functioned in similar ways. The majority of debitage appears to be locally derived from the gravels of the Luckiamute River and nearby Willamette River. Flake size measurements suggested that obsidian pebbles measuring less than 3 cm long were collected from the river gravels and reduced using bipolar flaking techniques.

At 35-PO-15, the 6.7 cubic meters of excavated fill yielded 2,151 pieces of debitage, as well as 53 chipped stone and eight groundstone tools and fragments. The debitage includes 292 (13.6%) obsidian, 1,761(81.9%) chert and 98 (4.6%) basalt fragments. Of the pieces of obsidian debitage, 22.6% were cortex fragments, while the rest were interior flakes. Some 12.7% were less than 0.5 cm in length, 58% were between 0.5 and 1 cm long, 27% were 1-2 cm long, and less than 3% were longer.

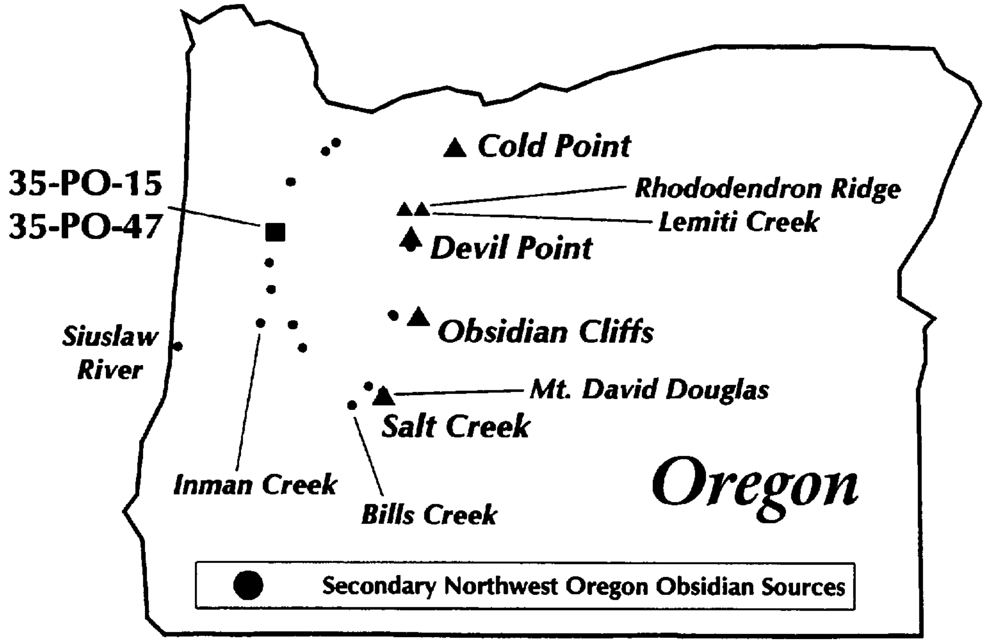

Figure 1. Locations of 35-PO-15 and 35-PO-47, western Oregon primary obsidian sources, and secondary deposits of obsidian correlated with the Inman Creek A and B source varieties.

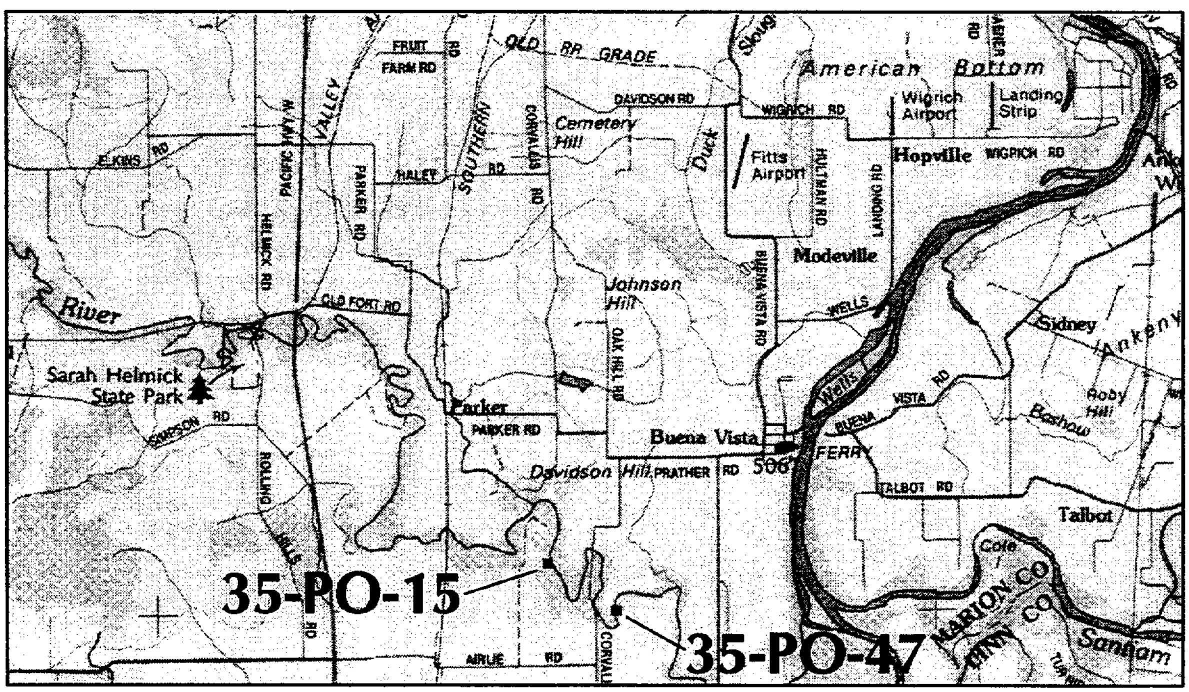

Figure 2. Locations of 35-PO-15 and 35PO-47 on the Luckiamute River (from DeLorme 1991).

The 7.0 cubic meters removed from 35-PO-47 produced some 1,796 pieces of debitage, of which 259 (14%) were obsidian, 1,416 (79%) were chert and 121 (7%) were basalt. In addition, some 39 chipped stone tools and fragments were recovered. No ground stone tools were recovered from the excavations, although surface fragments were found. Of the obsidian debitage, 9% were cortex flakes, while 91% were interior flakes. Ten percent of these obsidian flakes were less than 0.5 cm long, 61% were between 0.5 and 1 cm long, 29% were between 1 and 2 cm long and less than 1% were longer.

Artifacts Selected for Trace Element Analysis

The 14 artifacts selected for analysis consisted entirely of obsidian debitage (Table 1). All flakes were translucent or transparent and exhibited a glassy luster. Cortex was not present on any of the artifacts.

Based on the promising results of previous petrographic and trace element investigations of Willamette Valley artifacts and obsidian sources (Skinner 1986, 1991; Skinner et al. 1995a,

Table 1. Obsidian samples selected for AAS trace element characterization studies.

Site	Sample No.	Unit	Level	Max. Diam.	Inclusion Type	Predicted Source [A]
35-PO-15	15/A-2	A	2	1.4	None	–
35-PO-15	15/C-2	C	2	1.5	Microphenocrysts	Inman Creek A/B
35-PO-15	15/E-2	E	2	1.2	None	–
35-PO-15	15/E2-1	E2	1	2.7	Microphenocrysts	Inman Creek A/B
35-PO-15	15/E2-2	E2	2	3	Microphenocrysts	Inman Creek A/B
35-PO-15	15/E2-6	E2	6	1.8	None	–
35-PO-15	15/E2-8	E2	7	1.4	Microphenocrysts	Inman Creek A/B
35-PO-15	15/Z-1	Z	1	1.7	None	–
35-PO-47	47/5-4	5	4	1.2	Microphenocrysts	Inman Creek A/B
35-PO-47	47/7-6	7	6	1.4	Microphenocrysts	Inman Creek A/B
35-PO-47	47/8-2	8	2	1.1	Microphenocrysts	Inman Creek A/B
35-PO-47	47/8-4	8	4	1.6	Microphenocrysts	Inman Creek A/B
35-PO-47	47/9-3	9	3	1.2	Microphenocrysts	Inman Creek A/B
35-PO-47	47/29-5	9	5	1.3	Microphenocrysts	Inman Creek A/B

[A] Source was visually predicted due to presence of microphenocrysts.

1995b, 1996), we also attempted to predict the geochemical source of each artifact based solely on the visual characteristics of the glass. Obsidian correlated with the Inman Creek sources, particularly the Inman Creek A source group, often exhibits a "flawed" surface texture. This visually distinctive and easily recognizable surface texture is the result of the presence of small inclusions of microscopic to near-microscopic phenocrysts in the glass. These microphenocrysts have not been observed in artifacts or source material correlated with Obsidian Cliffs, the other major source group identified among Willamette Valley obsidian artifacts. Previous trace element studies suggest that the unique visual presence of the flawed surface texture in artifacts from Willamette Valley archaeological contexts can be used to reliably identify the origin of some artifacts. In other words, while the *presence* of microphenocrysts strongly points to the origin of an artifact as one of the Inman Creek source groups, the *absence* of this attribute cannot be used to assist in the identification of the source.

Ten of the 14 artifacts selected here for trace element analysis contained these microphenocrysts and, prior to AAS analysis, were predicted to belong to one of the Inman Creek source groups.

Western Oregon Obsidian Sources

Five geochemical sources of obsidian are indigenous to the Willamette Valley and Western Cascades of northwestern Oregon: Obsidian Cliffs, Inman Creek A, Inman Creek B, Devil Point, and Cold Point (see Figure 1).

Obsidian from the Obsidian Cliffs and Inman Creek sources is widely distributed in secondary alluvial deposits throughout northwestern Oregon (White 1974, 1975; Skinner 1983, 1986, 1991). The primary source for the Inman Creek A group, first recognized in the stream gravels of Inman Creek in the southwestern Willamette Valley, has been located in the Mt. David Douglas vicinity of the central Western Cascades. The source vent for the Inman Creek B source glass remains unidentified although the geographic distribution of characterized source samples and artifacts suggests that its location is also in the Mt. David Douglas area. Distribution studies of artifacts from the Devil Point source indicate that its prehistoric use was limited primarily to the local region surrounding the source (Skinner 1997a). The geology and geochemistry of these sources have been described by Anttonen (1972), Skinner (1983, 1986, 1991, 1997a, 1997b), and Hughes (1993). The northernmost obsidian source identified in the Oregon Cascades, the Cold Point source, is found in the Badger Creek Wilderness near Mt. Hood.

Several other sources of obsidian-like toolstone, the Clackamas River, Rhododendron Ridge, and Lemiti Creek sources (see Figure 1), are better described as glassy rhyolites than true obsidians. Like obsidian, these gray glassy rhyolites can also be geochemically characterized. Prehistoric use of the Clackamas River source, known only from characterized artifacts, appears restricted almost entirely to the Clackamas River drainage of the Western Cascades and eastern Willamette Valley (Woodward 1974; Roulette et al. 1996). Although the Cold Point, Rhododendron Ridge, and Lemiti Creek sources have only recently been identified, trace element studies of artifacts from the Mt. Hood and Willamette national forests indicate that it is likely that prehistoric use of toolstone from those sources was relatively limited.

Concurrent with the investigation reported here, geologic samples from the Inman Creek source groups and Obsidian Cliffs were also analyzed with AAS methods (see Appendix). These samples provided the geochemical source database with which the analyzed Polk County artifacts were compared. Artifacts from the Devil Point and Cold Point sources have not been reported from the central Willamette Valley and geologic samples from those sources were not included in our small source reference database. Although trace element data derived from X-ray fluorescence analysis of western Oregon geologic samples was also available (Skinner 1983, 1986; Hughes 1993), we noticed some potentially significant intermethod or interlaboratory differences in the results obtained by the different analytical methods. Because of this, it was necessary to construct a separate AAS source reference database with which to compare characterized archaeological samples.

Atomic Absorption Trace Element Analysis of Obsidian Artifacts

Although AAS has been only occasionally employed for obsidian provenience studies, the method has proven adequate for the task in previous investigations (Wheeler and Clark 1977; Hatch et al. 1990).

Atomic Absorption Analysis: Atomic absorption spectrometry (AAS) is one of several techniques of atomic spectroscopy that can be used to determine the trace element composition of analyzed samples. Originally used by astronomers to identify metals in the atmosphere of the Sun and other stars, atomic absorption spectrometry has enjoyed considerable popularity in geochemical studies since the 1960's. Rapid, sensitive, and inexpensive determinations of a wide spectrum of elements in a variety of different materials have resulted in the widespread availability of AAS facilities. Atomic absorption methods and instrumentation are widely described in the literature and the reader is referred to Johnson and Maxwell (1982) and Viets and O'Leary (1992) for further details.

Sample Preparation: Approximately 250 mg of obsidian was removed from each obsidian artifact (in some cases this comprised the entire item) and was ground by hand to a fine powder in mullite alloy mortar and pestle. The powdered sample was packaged in a polystyrene vial and delivered for analysis to the Center for Volcanology Atomic Absorption Laboratory, University of Oregon.

Results: The results of the trace element analysis of the obsidian debitage from the two sites are presented in Table 2. All artifacts were correlated with one of the two Inman Creek geochemical source groups. All of the visually characterized obsidian flakes were, of course, correlated with the Inman Creek source groups (Inman A = 8; Inman Creek B = 2).

Discussion: It is clear from the results of the current investigation and previous archaeological research that AAS methods are very suitable for the characterization of archaeological obsidian. In the investigation reported here, the trace element content of the 14 artifacts from 35-PO-15 and 35-PO-47 were compared with the composition of other western Oregon obsidian source reference standards analyzed by the Center for Volcanology Atomic Absorption Laboratory. Eleven of the artifacts were correlated with the Inman Creek A source; the remaining three items were assigned to the Inman Creek B source. The two geochemical source groups were easily distinguishable from Obsidian Cliffs, the other geologic source of obsidian often identified at Western Oregon archaeological sites. Subsequent X-ray fluorescence analysis of geologic samples from other western Oregon sources indicate that they are easily distinguished from the Inman Creek and Obsidian Cliffs source groups on the basis of their trace element content.

The advantages of AAS for the trace element characterization of obsidian artifacts were apparent during this investigation – the method was easily available, inexpensive, rapid, and produced accurate quantitative measurements of useful trace elements. The disadvantages of the method were equally apparent – AAS methods require the destruction of a small portion of the sample and a comparable geochemical source reference database was nonexistent.

As mentioned previously, the problem of interlaboratory or intermethod comparability also became apparent during the investigation. Several of the same glass nodules that were analyzed by AAS in the current investigation were also analyzed using non-destructive X-ray fluorescence (XRF) analysis methods. The results of these analyses, to be reported elsewhere (Skinner n.d.), indicate that zirconium abundances determined by XRF are significantly and systematically larger than those resulting from AAS methods. These differences do not prevent the use of either XRF or AAS techniques for the purpose of artifact provenience studies, but do limit the use of resultant trace element data. In the current investigation, for example, we had to construct an AAS reference database with which to compare analyzed artifacts. This proved to be a relatively straightforward procedure in the Willamette Valley, where only a few sources of natural glass are known to have been typically prehistorically utilized, but could prove problematic in more complex geographic areas.

Table 2. Results of AAS analysis of obsidian artifacts from 35-PO-15 and 35-PO-47.

Provenience		Trace Element Composition (parts per million)									Geochemical Source Group
Site	Sample No.	Ba	Co	Cr	Cu	Li	Ni	Rb	Sr	Zr	
35-PO-15	15/A-2	781	1	6	5	38	6	88	109	50	Inman Creek B
35-PO-15	15/C-2	730	4	5	5	36	3	80	139	54	Inman Creek A
35-PO-15	15/E-2	784	4	5	4	36	4	81	135	54	Inman Creek A
35-PO-15	15/E2-1	744	1	6	6	37	4	88	104	49	Inman Creek B
35-PO-15	15/E2-2	739	4	4	5	36	4	80	136	55	Inman Creek A
35-PO-15	15/E2-6	735	4	4	5	35	3	80	141	54	Inman Creek A
35-PO-15	15/E2-8	791	1	5	4	40	6	86	101	49	Inman Creek B
35-PO-15	15/Z-1	772	4	6	4	34	4	76	136	53	Inman Creek A
35-PO-47	47/5-4	772	2	4	4	35	6	80	142	57	Inman Creek A
35-PO-47	47/7-6	837	4	3	4	35	6	80	140	54	Inman Creek A
35-PO-47	47/8-2	806	4	3	4	35	4	79	142	55	Inman Creek A
35-PO-47	47/8-4	828	2	3	4	36	6	81	136	53	Inman Creek A
35-PO-47	47/9-3	758	4	3	5	34	6	80	136	53	Inman Creek A
35-PO-47	47/29-5	808	4	3	4	31	6	77	145	55	Inman Creek A

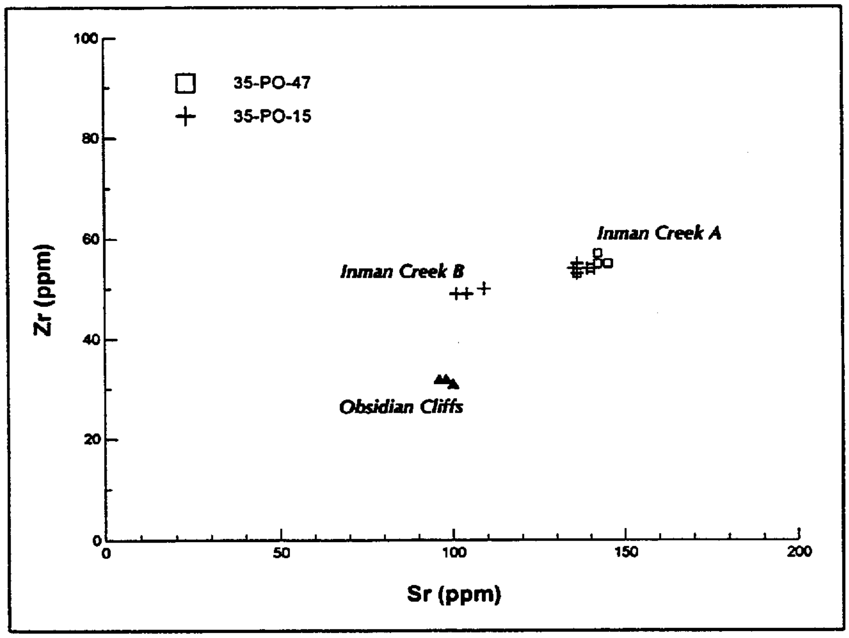

Figure 3. Scatterplot of strontium (Sr) versus zirconium (Zr), for artifacts from 35-PO-15 and 35-PO-47 and major western Oregon obsidian sources.

Conclusions

Given some limitations, i.e., destructive sample analysis, potential problems with intermethod or interlaboratory comparisons of trace element data, and undeveloped source reference databases, AAS methods show considerable utility for the geochemical analysis of obsidian artifacts. In a relatively simple obsidian source procurement region such as in the Willamette Valley, AAS can prove to be a valuable adjunct to other geochemical characterization methods. The elements rubidium and strontium were found to be particularly useful in distinguishing among different western Oregon obsidian sources.

The successful megascopic identification of artifacts from the Inman Creek source groups in the current investigation demonstrates the potential of visual characterization methods for artifacts originating from Willamette Valley sites. Visual obsidian source identification methods could be used independently or as an adjunct to more traditional trace element techniques. The occurrence of nodules of obsidian near the mouth of the Siuslaw River at the central Oregon Coast also suggests the utility of visual characterization methods in that region as well.

The results of the current investigation, when combined with extant trace element studies of Willamette Valley artifacts, continue to demonstrate the widespread prehistoric use of the two Inman Creek source varieties throughout northwestern Oregon. Although many areas of the Willamette Valley still lack obsidian provenience studies, we suspect that obsidian from the two Inman Creek groups was widely utilized in the Valley. The results also support our contention that the visual characteristics of artifact obsidian from Willamette Valley sites may be cautiously used to predict the presence of glass from the Inman Creek sources.

Acknowledgements

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Appendix: Results of AAS Analysis of Geologic Samples from the Inman Creek and Obsidian Cliffs Obsidian Sources, Western Oregon

Sample	Trace Element Composition (parts per million)									Source Group
	Ba	Co	Cr	Cu	Li	Ni	Rb	Sr	Zr	
BILLC-1	763	2.3	5	5	39	4	86	110	50	Inman Creek B
BILLC-2	786	2.3	5	5	35	6	85	141	54	Inman Creek A
BILLC-4	772	2.3	5	5	39	4	93	115	50	Inman Creek B
INM-1	767	21	5	5	39	9	93	115	48	Inman Creek B
INM-2	791	24	5	5	36	4	83	151	53	Inman Creek A
INM-3	791	23	5	5	35	4	82	141	54	Inman Creek A
INM-5	758	9.4	4	5	35	4	83	143	53	Inman Creek A
INM-11	739	20	4	5	38	4	90	106	49	Inman Creek B
INM-12	767	3.5	27	6	35	4	79	140	52	Inman Creek A
SACR-2	791	3.5	4	5	35	4	83	136	54	Inman Creek A
SACR-3	763	2.3	4	5	35	4	82	144	54	Inman Creek A
SACR-4	758	2.3	5	5	38	4	81	137	53	Inman Creek A
SACR-8	739	3.5	4	5	37	6	82	135	55	Inman Creek A
SIU-1	763	3.5	37	11	36	8	82	127	54	Inman Creek A
SIU-3	800	3.5	5	5	37	4	82	136	54	Inman Creek A
SIU-4	805	3.5	4	5	35	4	82	129	57	Inman Creek A
SIU-5	781	3.5	4	5	36	4	84	137	54	Inman Creek A
VRS-1	753	2.3	6	5	34	6	76	141	54	Inman Creek A
VRS-2	735	2.3	5	5	35	6	79	144	54	Inman Creek A
OBC-2	805	12	5	5	35	4	76	96	32	Obsidian Cliffs
OBC-3	847	11	4	6	38	6	79	98	32	Obsidian Cliffs
OBC-4	842	3.5	4	5	36	6	76	100	31	Obsidian Cliffs

BILLC	Bills Creek Site, 35-LA-519, Lane County, Western Cascades, Oregon; naturally occurring nodules collected at site.
INM	Inman Creek, Lane County, southwestern Willamette Valley, Oregon; collected from stream gravels.
SACR	Salt Creek, Lane County, Mt. David Douglas area, Western Cascades, Oregon; collected at source.
SIU	Siuslaw River, central Oregon Coast.; nodules collected from gravel bar.
VRS	Vine Rockshelter Site, 35-LA-304, Western Cascades, Oregon; cores used to characterize possible local source.
OBC	Obsidian Cliffs, Lane County, High Cascades, Oregon; collected at primary source.