Chemical Differentiation of Obsidian within the Glass Buttes Complex, Oregon

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Two hundred twenty-five source samples from the multi-component obsidian source at Glass Buttes, Oregon were characterized by neutron activation analysis to determine the number of chemical groups present. Seven geochemical groups were found within the Glass Buttes complex. An abbreviated neutron activation analysis procedure previously used to differentiate between obsidian sources in Mesoamerica was also successful in separating obsidian from different outcrops at Glass Buttes. Thirty-one artifacts from the Robins Spring site on Glass Buttes were also analysed. The abbreviated NAA procedure was also successful at assigning the artifacts to the different subsources at Glass Buttes.

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Introduction

A number of analytical methods have been employed with success to characterize the compositions of source and artifact materials made from obsidian (i.e., rhyolite glass) over the years. These methods include optical emission spectroscopy (OES) (Cann & Renfrew, 1964), proton induced X-ray emission (PIXE) (Nielson et al., 1976), back-scattered electron imaging (Burton & Krinsley, 1987), neutron activation analysis (NAA) (Gordus, Wright & Giuffri, 1968), X-ray fluorescence (XRF) (Nelson et al., 1975), and atomic absorption spectrophotometry (AAS) (Wheeler & Clark, 1977). Although the methods were different, the goal was always the same, to take advantage of the characteristics of obsidian (i.e., the usual conditions of intra-source chemical homogeneity and inter-source heterogeneity) in order to assign artifacts to specific sources. The successes of early studies were, however, frequently compromised by analyses that involved small numbers of source samples or the measurement of only a few elements. The problem was further intensified when Bowman, Asaro & Perlman (1973) showed that some sources were intrinsically inhomogeneous and when Hughes (1988, 1994) showed that certain source areas were composed of a number of chemically distinct “subsources”.

It became evident to a number of obsidian researchers (Glascock, Braswell & Cobean, 1998; Shackley, 1995) that in order to properly characterize obsidian source areas it was necessary to undertake a careful geological and geochemical study of the region first. This included finding the geographical limits of the obsidian zone, taking careful note of where specimens were collected, and making sure enough samples were characterized to be able to make statistically valid statements about the composition of obsidian from a source. The techniques also began to measure greater numbers of elements (i.e., 10–25 versus 2–3) to use for differentiation and to determine the “best elements” rather than be limited to the most convenient elements available to the analytical method employed.

It is important to determine as many elements as possible to differentiate between chemical groups (i.e., geographic source areas). Comparisons between source areas in different regions will not necessarily use the
same elements for the most effective separation. One never knows a priori which elements will work best. Elements that work well in one region may be unsuccessful in another region. Therefore, source samples should always be analysed for all elements determinable by the method.

On the other hand, when analysing artifacts it should only be necessary to measure the number of elements which provide a correct (and high probability) assignment to a particular geochemical fingerprint. Typically as few as three or four of the “best elements” (Hughes & Smith, 1993) will be sufficient to reliably determine the source.

The state of Oregon contains many centres of rhyolitic volcanic activity and has a large number of obsidian sources. The number is estimated to be well in excess of 100 geochemically distinct obsidian sources. Some of these sources may not be artifact quality or may not have been accessible to prehistoric populations but this still leaves a significant number of possible sources from which artifacts may have originated. Skinner (1983) characterized several sources in Oregon by X-ray fluorescence (XRF); however, the samples were from definite quarries exploited by Native Americans and did not completely characterize the source itself. There have been other limited characterization studies of source regions (e.g., Hughes, 1986) but none have been conducted on a large scale to cover the entire state.

In most archaeological provenance studies, Glass Buttes has been treated as a single geochemical source (Skinner, 1983, 1995; Hughes, 1986). However, research reported by D’Auria, James & Godfrey-Smith (1992) and Godfrey-Smith et al. (1993) suggests that multiple geochemical sources are present. The study reported here was undertaken as part of a large effort to identify, locate, and characterize as many obsidian source areas in Oregon as possible using NAA (Ambroz, 1997). At the present time, 42 different geochemical fingerprints (i.e., source groups) have been identified in our NAA studies. In excess of 100 different source groups have been found by XRF analysis of obsidian source material (unpublished research results, Northwest Research Obsidian Studies Laboratory). The greater number of source groups determined by XRF is due to the much larger number of source samples from Oregon that have been analysed by XRF. As demonstrated by the current investigation, some of these, including the Glass Buttes source area of central Oregon, are complex, multi-component sources and need to be examined in greater detail.

Two hundred twenty-five source samples from 26 different sampling locales were collected around Glass Buttes over a two-day period in June 1996. At each source locale approximately 20–30 fist-sized pieces of obsidian were collected at random to represent that outcrop. Samples were divided between the two laboratories to allow chemical analysis by both NAA and XRF. Additional source samples reported here were obtained during earlier sampling trips by C. E. Skinner. The individual sampling locales were recorded geographically by longitude and latitude with the use of a Global Positioning System (GPS). We present here the results of NAA studies of obsidian associated with the Glass Buttes source complex. Subsequent field work and XRF trace element studies of the Glass Buttes obsidian sources are still underway and will be reported elsewhere when they are completed (Skinner, 2000).

**Background**

**Glass Buttes**

Glass Buttes is a large bimodal volcanic centre located approximately 80 km west of Burns, Oregon and just south of U.S. Highway 20 in the northeast corner of Lake County, Oregon (Figure 1). The complex is approximately 20 km long and 10 km wide and trends generally to the southeast. Within the High Lava Plains is a zone of silicic volcanic centres trending approximately N75°-80°W beginning at Duck Butte in the east and ending with Newberry Crater in the west. Glass Buttes is a part of this trend, intersecting with the Brothers Fault Zone (a series of faults trending N-S). This zone of silicic centres is additionally interesting because of a westward progression of decreasing age for each complex (MacLeod, Walker & McKee, 1975).

Obsidian associated with the Glass Buttes complex has yielded K-Ar ages ranging from 5.04 ± 0.75 to 6.5 ± 1.3 million years (Fiebelkorn et al., 1983 and Godfrey-Smith et al., 1993).

Waters (1927) conducted the first significant geological study of Glass Buttes. He identified three periods of extrusion of both basalts and what he termed as andesites. He described the obsidian as boulders in dry stream channels and as loose blocks in pumiceous sand but rarely found in place (Waters, 1927). Since that time, Glass Buttes has been explored for its geothermal potential (Johnson & Ciancanelli, 1984), cinnabar (mercury) deposits, and precious metal content (Berri, 1982; Johnson, 1984).

Previously, Glass Buttes was mined for its cinnabar deposits, but at the present time all mining activity has ceased. Berri (1982) studied the petography of part of Glass Buttes, from its easternmost edge to Little Glass Buttes. She found that the rhyolitic volcanism began between about 9 million years ago and 5 million years ago.

Although most of the rocks of the Glass Buttes complex are silicic rhyolite and rhyodacite flows and tuffs (that include obsidian), this central complex is surrounded by earlier and later basalt and andesite flows. The stratigraphy of the rhyolites is complicated because the complex was built by successive eruptions of small volume (Berri, 1982).

Berri mentions obsidian only when discussing the Little Glass Buttes area. She identified three separate
units around Little Glass Buttes and Obsidian Hills (to the north) which overlap and are overlapped by basalts. Johnson (1984) continued some of the work started by Berri, but concentrated mainly on the hydrothermal alteration that took place at Glass Buttes. Roche (1987) also built on the work of Berri. He performed a greater number of analyses on the obsidian, but he only analysed samples from the eastern areas.

Obsidian of extremely high quality is found at Glass Buttes. It also comes in a large variety of colours including black, mahogany, snowflake, and rainbow. It is highly prized by gem collectors and flint knappers; during the summer months it is quite common to find large numbers of people exploiting the various outcrops. Obsidian from Glass Buttes was widely used by Native Americans. There are several springs on the complex, each of which has an archaeological site associated with it (Zancanella, pers. comm.). Although Glass Buttes was a major regional prehistoric source of natural glass (Skinner, 1995), the obsidian was also used at sites distant from the source area. For example, Hughes (1990) found that many of the large bifaces found at the Gold Hill archaeological site (about 300 km from Glass Buttes) in Oregon originally came from Glass Buttes obsidian. Glass Buttes obsidian has also been found at the Gunther Island archaeological site in northwestern California (Hughes, 1978) and has been reported from as far north as British Columbia, Canada (Carlson, 1994). Certain varieties (e.g. red-coloured) may have been highly prized and traded great distances for ceremonial purposes (Zancanella, pers. comm.). It is very likely that there are many other archaeological sites where studies have not been made that also contain artifacts made from Glass Buttes obsidian.

Robins Spring site
Thirty-one artifacts collected from the Robins Spring site were subjected to both short and long neutron activation analysis irradiations. This archaeological site is located within the complex and near Glass Buttes proper (see Figure 1). The dimensions of the site are about 1.5 km north-south and 0.8 km east-west (Zancanella, pers. comm.). A large hill on the east is the main source of the obsidian. Chipped stone covers most of the site and some ground stone is also found. Certain areas show more advanced production of bifaces; although no diagnostic artifacts have been found (Zancanella, pers. comm.). The artifacts submitted for analysis comprise a random surface sample from across the site and are intended to provide a preliminary picture of obsidian source use at this location.

Sample Preparation and Laboratory Analysis
After the source samples arrived in the lab, a minimum of six pieces from each sampling location were washed with distilled water and crushed into smaller pieces to obtain clean interior fragments (e.g., 10–25 mg pieces) for analysis by NAA. If significant compositional variability was suspected or found after analysing these initial samples, additional samples were prepared. The artifacts were washed and a small portion was removed...
with a trim saw. The removed portion was also crushed into smaller fragments for irradiation. The sample for short irradiation typically consisted of 100 mg of fragments. Each sample was placed into a small polyethylene vial and fixed to the bottom using clean styrofoam plugs. Samples for long irradiation, weighing about 300 mg, were placed in high-purity quartz vials and were sealed under vacuum.

The polyethylene vials containing samples for short irradiation were placed into polyethylene rabbits two at a time and irradiated in the pneumatic tube system. They were irradiated for five seconds in a neutron flux of $8 \times 10^{13}$ n cm$^{-2}$ s$^{-1}$. Sample irradiations were followed by a 25-minute decay period and 12-minute gamma count with a high-purity germanium detector and standard counting software. The elements measured following short irradiation were Ba, Cl, Dy, K, Mn, and Na.

The quartz vials containing samples for long irradiation were rolled up in batches of 30 samples and six standards and were irradiated in aluminium cans near the reactor core for 70 h at a neutron flux of $5 \times 10^{13}$ cm$^{-2}$ s$^{-1}$. After irradiation they were allowed to decay for approximately 7–8 days and were counted for 2000 seconds each (mid-count). The elements measured from the mid-count were Ba, La, Lu, Nd, Sm, U, and Yb. Another final gamma count was made after about 4–5 weeks decay for 10,000 seconds (long count). The elements measured from the long-count were Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr.

### Results

The data from the source samples was examined by creating a series of bivariate plots. The examination found that the incompatible elements (i.e., K, Rb, Sr, Zr, Cs, Ba, REE’s, Hf, Th, and U) were best at revealing patterns to separate the source groups within the obsidian data set. The incompatible elements are those which commonly substitute into the structures of early crystallizing minerals. As the magma is evolving, trace elements are preferentially concentrated in the liquid phase because they have too large an ionic radius or are too highly charged to enter the crystal structure (Conrad, 1984; Fink & Manley, 1987; Hildreth, 1979, 1981; Mahood & Hildreth, 1993).

In this study, two of the most sensitive and best discriminating elements available by neutron activation analysis data were thorium and europium. As shown in Figure 2, a plot of Eu versus Th reveals seven different chemical fingerprints for Glass Buttes that are well separated from one another. The mean element concentrations for each of the geochemical source groups found in this study are shown in Table 1.

It is interesting to note that the fingerprints that are closest to each other geochemically are also near each other geographically (e.g., groups C and F and groups D and E) as shown in Figure 1. The fingerprints also show some trends. From east to west the elements cesium and thorium show a very general decrease in value. On the other hand, europium follows a general trend of increasing values from east to west.

Once the fingerprints of the subsources were established, the data from the 31 analysed artifacts was also examined and compared to the trace element composition of the sources. As shown in Figure 3, all of the artifacts were assigned to subgroups from within the Glass Buttes complex except a single artifact that matched the Yreka Butte source (an obsidian source found about 5–8 km west of Glass Buttes).

The artifacts were also successfully assigned to sources using an abbreviated-NAA method (i.e., short irradiation only) that we originally developed for sources in Mesoamerica (Glascock et al., 1994) (Figure 4). Although groups A and B overlap slightly in this plot, this is not a problem because they are very different for barium, an element also measured by the short irradiation procedure.

### Summary

Neutron activation analysis of source samples from the Glass Buttes rhyolitic complex revealed the existence of seven different geochemical source groups within the complex. These fingerprints were also proven to be separable when employing an abbreviated-NAA procedure. Artifacts from an archaeological site on Glass Buttes were successfully assigned to the fingerprints using the abbreviated method. The ability to use only the short irradiation will prove to be beneficial by saving both time and expense.

Glass Buttes is a complex of many obsidian flows. A very large survey of the area was able to distinguish the seven groups but there may still be additional areas that need to be sampled. The geochemical and source information amassed thus far are valuable to
archaeologists who wish to analyse artifacts believed to have originated at Glass Buttes. The data will also likely be useful to geologists because of the trending patterns within the complex.

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References


