PROVENANCE SOURCING OF OBSIDIAN ARTIFACTS FROM MANAGUA, NICARAGUA, USING TRACE ELEMENT GEOCHEMISTRY

by

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ABSTRACT

Provenance studies are undertaken by archaeologists and other archaeoscientists to determine the source(s) of the materials from which artifacts were fashioned in ancient times, often using chemical data. The provenance information allows them to understand the movement of these materials over time and space, thereby gaining an understanding of relationships among peoples, including trade routes and exchange practices. Lithic artifacts, along with ceramic materials, are often the most abundant artifacts found in excavations. A number of lithic materials have been the subject of geochemical provenance studies, including chert, flint, andesite, basalt, and obsidian. Each of these materials is unique, but not necessarily well-suited for geochemical provenance studies. Obsidian, however, is nearly ideal: it forms in geologically specific locales, thus the number of possible sources is somewhat limited; and, it is formed when magma cools quickly, thus the chemistry of the entire flow is the same, or very nearly so.

Obsidian geochemical provenance studies are typically performed in 2 different, though related, ways: 1) comparing compositional data for artifacts to the ranges of compositions for potential sources, with those artifacts falling within the range for a certain source considered to have originated from that source; and, 2) plotting (element versus element plots) data for both artifacts and possible source samples and comparing them, with those artifacts falling within the "envelope" defined by the sample population for a certain source considered having originated from that source. The second method is utilized in this study, using trace elements. A drawback to both methods is that they can possibly yield ambiguous or erroneous results when comparing sources whose compositions overlap for numerous elements, a situation that may not be avoided in some studies, and indeed, is encountered here. However, trace elements have not only been successful for determining provenance in previous studies, as they are often among those elements that show significant differences between sources, even those with otherwise similar chemistry, but are also used successfully here.

This study involved the determination of provenance for 96 obsidian artifacts (debitage fragments, unusable pieces remaining from the manufacture of usable tools and/or weapons from a larger piece of material) excavated from 5 small archaeological sites located in and near metropolitan Managua, Nicaragua. Also presented are analytical results obtained here for 4 other artifacts from these sites: 2 pottery shards, and 2 other lithic pieces (1 broken blade of silicified conglomerate, and 1 quartz pebble; these both are also debitage fragments). Trace elements, in element versus element plots, were utilized to compare compositions of obsidian from all known obsidian sources located in Central America, and select sources in Mexico, to the analyses for the 96 obsidian artifacts. The chemical analyses of the 96 obsidian (and 4 other) artifacts were obtained via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) during this study, while the analytical data for the sources was gleaned from a number of sources (see Chapter 5). Five obsidian artifacts were definitively provenanced (showed very strong correlation) to 2 source materials (4 artifacts (LP-03, LP-05, UNI-01, and MO-04) with Ixtepeque, Guatemala, and 1 (CS-02) with La Esperanza, Honduras), while the remaining 91 obsidian artifacts were less definitively provenanced (showed weaker correlation) to 3 source materials (1 artifact (CS-37) to Guadalupe Victoria, Mexico, and the remaining 90 to the often overlapping sources of Güinope, Honduras, and Jalapa, Guatemala). Nine trace elements proved particularly useful in this study (Ba, Ce, Cs, La, Rb, Sr, Ta, Th, and U), and 1 major element (Fe) and 1 minor element (Mn) played invaluable roles in providing separation between 2 sources with very similar chemistry.

In addition, "droplets" of previously-molten copper were discovered attached to 5 of the obsidian artifacts studied here, with all these artifacts excavated from just 1 of the archaeological sites. Their external morphology is drops and splatters, while their internal morphology is typical of quickly-cooled molten material, with dendrites, segregated material, and trapped gas bubbles. Overall, they are nearly pure copper (<1% Fe), although the dendrites and segregated material are slightly enriched in Fe (~2%), with no other elements detected (via Electron Microprobe) in any of the phases. Little other evidence has been found in this area of Central America of copper-working for this timeframe (~300-1200 AD); additionally this is the first known discovery of evidence of the concurrent working of both obsidian and molten copper for this area.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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CHAPTER 1
INTRODUCTION

Geochemical provenance studies involve tracing artifacts back to their source materials by use of geological, geochemical and archaeological information. Information obtained from lithic artifacts and their source materials are used by archaeologists for interpreting trade, exchange, and other movement patterns among prehistoric peoples (for example: Jackson and Love 1991; Negash and Shackley 2006). Lithic artifacts are often the most abundant artifacts found in excavations, aside from those comprised of pottery and/or ceramics, due to their hardiness and persistence (often remaining intact or mostly undamaged) despite being subjected to the often extreme environments of burial and weathering. Numerous types of lithic materials have been the subject of geochemical provenance studies, including chert, flint, andesite, basalt, and obsidian (Tykot 2003). Results obtained for these materials have ranged from good to poor, as these materials, although each unique, are not necessarily well-suited for geochemical provenance studies. Obsidian, however, is nearly ideal for such studies: 1) obsidian forms in geologically specific locales, often in rhyolite dome sequences, thus the number of possible source materials is somewhat limited, and it has unique textures, structures and ranges of chemical composition (for example: Best 2003; Bouška 1993; Hall 1996; Wilson 1989); 2) obsidian artifacts are often recovered from archaeological sites showing little physical or chemical alteration despite burial for hundreds, even thousands, of years; and, 3) obsidian was widely used by prehistoric peoples for manufacturing tools, weapons and other items, and thus is a common artifact material.

Obsidian is a naturally-occurring volcanic glass, and often forms when silica-rich melt is quenched from magmatic to solid state (see as example references for this brief discussion: Best 2003; Bouška 1993; Hall 1996; Wilson 1989). This rapid cooling impedes crystal growth, and relatively few crystals form resulting in little or no chemical fractionation occurring between the solid crystalline phases and the liquid magma phase. Therefore the overall chemical composition of the obsidian will be very nearly that of the magma from which it solidified. Elements present in igneous rocks, including obsidian, are usually referred to in the following manner (see also Chapter 2): “major” elements are present in the highest concentrations (>1.0% by weight, as the bulk of a rock is usually made up such elements); "minor" elements are present in lower concentrations (0.1-1.0% by weight, as they usually comprise only a small amount of a rock); and, "trace" elements are present in the lowest concentrations (< 0.1% by weight, as they are present in usually only trace amounts). Many trace elements are also "incompatible" with the solid phases that are forming in a cooling magma, and are preferentially not incorporated into these phases; these "incompatible" trace elements thus continue residing in the remaining liquid magma as it cools and solidifies, and the liquid tends to become more concentrated in these elements over time.

The idea of tracing obsidian artifacts back to source obsidians using elemental compositions (even trace elements) is far from new. Obsidian geochemical provenance studies are typically performed in 2 different, though related, ways, using elemental compositions: 1) comparing artifact compositions to compositional ranges for potential sources (for example: Sheets et al. 1990; Sidrys and Kimberlin 1979; Stross et al. 1983); and, 2) plotting (element versus element) compositions for both artifacts and potential source samples (for example: Brown et al. 2004; Dahl et al. 1990). For both methods, those artifacts falling within the compositional range or the plotted "envelope" or ellipse (comprised of the plotted points plus an acceptable statistical variation or confidence interval) for a given source is thus determined to have originated from that source. Many studies use statistical schemes of some sort, some quite complicated, for grouping and/or separating data points, delineating between and/or defining source envelopes, and for providing more mathematical assurance of source assignments, especially when working with sources of similar chemistry. Often these source envelopes overlap for some elements, thus yielding possibly uncertain or indeterminate artifact source assignments; this is especially problematic for sources with similar chemistry, as numerous elements may have overlaps. This problem will likely grow larger over time, as the number of potential source obsidians increases with every new location found. However, trace elements, and especially incompatible trace elements, may be increasingly important for obsidian provenance studies: 1) trace elements are often among the elements showing some unique variation for a source, thus allowing for separation of sources of otherwise similar chemistry; and, 2) for future study (see

Chapter 7), possibly more definitive artifact assignments might be achieved via plotting incompatible trace element ratios (ratio versus ratio), as ratios of incompatible trace elements to one another are often quite constant (see for example: Allègre and Minster 1978; Arth 1976; Hanson 1980; Haskin 1984), thus such plots may show smaller and less scattered source envelopes than those seen in many element versus element plots.

This present study involved the identification of source materials for obsidian artifacts from Nicaragua using mainly trace element compositions. One hundred artifacts of unknown composition excavated from 5 small archaeological sites were studied here: 96 pieces were composed of obsidian (actually debitage fragments, which are unusable pieces remaining from the manufacture of usable weapons, tools or other items from a larger piece of material; Frederick Lange, verbal communication November 1999) and thus of primary interest here, with the other 4 comprised of 2 pieces of other lithic materials (also debitage fragments) and 2 pottery shards. Four of the sites were located in metropolitan Managua: Ciudad Sandino, Los Placeres, Universidad Nacional de Ingeniería (National Engineering University), and Villa Tiscapa. The fifth site consists of excavations on 2 small islands (Isla Honda and Isla Moyuá) in Lake Moyuá, ~72 km (~45 miles) NNE of Managua. The reader is referred to Lange (ed. 1995, ed. 1996) for more details regarding the archaeological sites and excavations.

In this study, compositional data for all known obsidian sources in Central America were compared to the chemical data obtained here for the 96 obsidian debitage pieces using element versus element plots; a select number of Mexican obsidian sources were also compared. The chemical data for the obsidian sources were gleaned from a number of sources (see Chapter 5). Nine trace elements were important in determining the source assignments (Ba, Ce, Cs, La, Rb, Sr, Ta, Th, and U), with 3 being particularly useful (Cs, Rb, and Th); the major element Fe and the minor element Mn also played an important role in distinguishing between 2 sources with similar chemistry. The plot of Rb versus Cs yielded distinct populations for Ixtepeque, Guatemala (IXT), San Martín Jilotepeque, Guatemala (SMJ), and La Esperanza, Honduras (ESP), although the sample populations for El Chayal, Guatemala (EC), Jalapa, Guatemala (JAL), and Güinope, Honduras (GUIN) did not resolve as clearly (Cs abundances overlapped, and Rb overlapped somewhat). The plot of Th versus Cs also yielded fairly well-separated populations for IXT, SMJ, and ESP, with EC and GUIN again still slightly overlapping for Cs abundances, but showing well-separated Th abundances, although GUIN and JAL still overlap quite a bit. Thus, with just 3 trace elements, 5 of the 6 most likely sources of obsidian for the artifacts studied here were delineated from one another. The remaining 2 that (often) overlapped (GUIN and JAL) could not be separated, and led to more tentative assignments for the artifacts which fell into that range of composition.

An unexpected, and possibly quite important, discovery coming out of this study is the presence of tiny droplets of copper metal attached to the surface(s) of just 5 of the 96 obsidian artifacts studied here, as presented in Aggen et al. (2000). All 5 of these artifacts were excavated from the Ciudad Sandino site, in metropolitan Managua, which consisted of 2 small excavations ~1 km apart (Frederick Lange, written communication 11/2/2000). From analyses of pottery and ceramics also recovered from the site, it was determined to be as old as ~500 BC to as recent as ~1520 AD (Keller et al. 1996:85, 92), and the strata from which the 5 artifacts retaining copper droplets were likewise determined to be ~300-1200 AD in age (Frederick Lange, written communication 11/6/2000). No other evidence of metal-working was found at this site, nor any of the other sites involved in this study (Frederick Lange, written communication 11/6/2000); however, all 5 sites were quite small, and could be considered "test pits" (Frederick Lange, verbal communication November 1999). There remains much more area in Central America yet to be explored, examined, and excavated, especially in Nicaragua and Honduras (Lange 1996a, 1992c; Willey 1984). Therefore an unknown amount of metal-working evidence may yet exist, still buried and awaiting discovery. It is hoped that further fieldwork will provide answers. The discovery of these copper droplets, along with the knowledge that the artifacts retaining them were derived from close-by sources, clearly implies that the working of obsidian and the working of molten copper were both being performed in the same place and at the same time. As there is currently a paucity of evidence regarding copper-working in prehistoric Nicaragua, indeed Central America (see for example: Lange 1996a; West 1994), the implications of this discovery may be quite important.

CHAPTER 2

OBSIDIAN FORMATION, COMPOSITION, AND USE

Obsidian is an ideal material for provenance studies. It forms in geologically specific locales, often in rhyolite dome sequences, thus the number of possible source materials is somewhat limited. It has unique textures, structures, and ranges of chemical composition, and is remarkably homogeneous chemically, thus each piece of obsidian removed (or artifact fashioned) from a given flow will have the same chemical composition as all others from that flow. Obsidian artifacts are often recovered from archaeological sites showing little physical or chemical alteration despite burial. And, obsidian was widely used by prehistoric peoples for the manufacture of tools, weapons, and other items, and thus is quite common as an artifact material.

Obsidian Formation

Please note that after the following discussions in this chapter, the term "obsidian" will be used throughout the remainder of this work in reference to natural volcanic glass of rhyolitic composition (high silica content), unless noted otherwise.

Obsidian is a naturally-occurring volcanic glass that forms in two main ways: 1) rapid cooling of lava, thus it generally comprises the upper (and often basal) parts of lava flows or domes (Bouška 1993; Hall 1996; Le Maitre 2002); and, 2) welding together of hot pyroclastic materials before they have completely cooled, or slower welding of such materials due to overlying pressure (Best 2003; Ross and Smith 1961; Sheridan 1979; Smith 1960; Wilson 1989). There are numerous other ways natural glasses can form, such as due to impacts from meteorites and the like (termed "impactites" or "tektites," or localized names such as "moldavites" found in Moldavia), due to lightning strikes ("fulgurites"), to such exotic means as melting of claystone during spontaneous coal fires ("porcelanites") (Bouška 1993). As these other glasses are usually too thin, too small, or of insufficient quality for use in fashioning tools, they are not discussed further here, save to mention that a number of "worked" (worked via knapping, and/or used by man) tektites and moldavites have been excavated from archaeological sites in Austria and Moravia, and on Luzon Island, Philippines (Bouška 1993:299).

Although commonly black or brown in color, obsidian of nearly every color has been found, including colorless, gray, blue-gray, gray-black, gray-green, purple-brownish, reddish, mahogany, and green (Bouška 1993:95-96). The color of a glass, natural or otherwise, results from the mixture of the visible colors of light that are not absorbed by the glass (Bouška 1993:61). Some obsidians have been noted to have a "silvery luster" (Bouška 1993:95), and this phenomena may likely be due to tiny gas bubbles trapped just under the surface of the obsidian, as was observed to be the cause of a similar such "surface" for one obsidian piece studied here (see Appendix C).

The reader is referred to Best (2003), Bouška (1993), Hall (1996), and Wilson (1989), as well as Jackson (1997), for the following discussions. Volcanic glass, often called "obsidian" no matter its composition, can form from the rapid cooling of lava of any composition. There are 2 main parameters which affect the thickness of the glassy layer that forms on a cooling lava: 1) the silica content of the lava (often the more important factor), and, 2) the rapidity of cooling. The higher the silica content of a lava, the higher its viscosity and the more slowly it flows, thus it will tend to pile up and form thick layers. In general, the most common volcanic glass composition is rhyolitic (felsic, or silica-rich; ≥66% silica by weight), with intermediate composition (dacitic through andesitic; <66% to >52% silica) less common, and basaltic composition (mafic, or silica-poor; <52% silica) least common. Fast cooling of lava impedes the movement of chemical components within it, thus slowing diffusion of such components to crystal nucleation sites, thereby impeding crystal nucleation and growth. Very fast cooling essentially "super-cools" the lava below the temperature at which these processes normally occur, thus many volcanic glasses have low to very low crystal contents.

Obsidian tends to form in significant amounts in geologically specific locales, where silica-rich magmas have erupted onto the surface, often resulting in the formation of rhyolite dome sequences. These sequences tend to be significant sources of obsidian, as the volume percent of material of sufficient quality for artifact manufacture to overall volume of material is generally significantly higher than that for natural glasses formed from lower silica lavas or by welding of pyroclastic materials. These dome sequences are essentially solidified piles of lava flows, composed of any number of successive layers of solidified crystallized and/or glassy materials, and are of varying height and areal extent depending on the overall volume of lava(s) extruded over time. The higher viscosity of high-silica lavas tend to constrain their ability to flow, thus these lavas tend to form thick flows of relatively small areal extent; in contrast, lower-silica, thus lower viscosity, lavas tend to flow easily, tending to form thinner volcanic flows of relatively large areal extent.

As lava cools, a surface rind or "crust" develops, as cooling occurs there first, and proceeds inward. Cooling crusts vary in appearance and texture depending on the gas content, viscosity, and chemical composition of the magma. These surface crusts are categorized according to their distinctive morphology, with the extremes being termed "pahoehoe," for smooth, ropy, or billowy surfaces, and "aa," for rough, jagged, spinose, or clinkery surfaces. As high silica content often leads to thick accumulations, this often results in blocky chunks to irregular fragments, with the cooling "crusts" ranging from ropy-looking, to polyhedral, to irregular, and even vesicular (with higher gas contents).

The reader is referred to Best (2003), Friedman and Long (1984), Hall (1996), Le Maitre (2002), Ross and Smith (1961), Sheridan (1979), Smith (1960), and Wilson (1989) for the following discussion. The dense obsidian-like material formed by welding of pyroclastic materials may more accurately be termed a "welded tuff," "welded ash flow," or similar such terms, but will be referred to here as "obsidian." The pyroclasts can be composed of numerous of types and sizes of material, ranging from tiny particles of volcanic ash (<2.0 mm in diameter; Jackson 1997), to pumice fragments of virtually any size, to the largest pieces called "bombs" (>64 mm in diameter; Jackson 1997); crystals (phenocrysts) formed prior to extrusion may also be among the welded materials. Often, the welding of the pieces is incomplete, with some space remaining between the pieces, and/or the cohesion of the welds may be low; the resulting obsidian-like material is often brittle and can break apart rather easily. However, some obsidian formed in this manner can be of high quality and virtually indistinguishable from obsidian formed directly from lava (see for example: Ross and Smith 1961:Figure 9). Overall, this type of obsidian deposit tends to be variable in quality, composition, size, thickness, areal extent, location, etc. An example of a possibly more homogenous deposit is the Alca obsidian deposit in Peru, for which at least 16 outcrops of obsidian (both as volcaniclastic flows and nodules in consolidated volcaniclastic tuff) were found over an area of 50 km^2 (Jennings and Glascock 2002).

Obsidian Composition

The reader is referred to Best (2003), Hall (1996), Wilson (1989), and Winter (2001) for general information regarding the following discussions. The fractionation of elements, especially trace elements, between the crystallizing minerals and the remaining liquid in a solidifying magma is an ever-expanding field of knowledge. Arth (1976) and Hanson (1980), as well as Allègre and Minster (1978) and Haskin (1984), are good summaries of the knowledge up that point, and still serve well today as introductory primers to the subject. Among the studies of this type that focused on magmas of higher-silica content are Hanson (1978) and Mahood and Hildreth (1983).

As a magma cools, the chemical components within it fractionate (divide) between the liquid and the forming crystals. At any given moment, the particular chemical components that are taken up into the crystallizing solids depend on 2 main factors: 1) the exact composition of the liquid; and, 2) the particular minerals that are growing (starting to nucleate and/or currently crystallizing). Other factors include the liquids' viscosity, density, temperature, water content, vertical and horizontal thickness, and rate of cooling, as well as whether the crystals are chemically isolated from the liquid or can still react with it, etc. Thus, as a given magma cools, its chemistry changes as components are removed from (and sometimes brought back into) the remaining liquid. Typically, though, concentrations of major elements such as Si and Al may not vary greatly, but trace element compositions can vary widely. In general, the more quickly a given magma cools, the more the chemistry of the last material to solidify is similar to that of the original magma, as it likely has not fractionated to a great degree. Obsidian, which forms by the rapid cooling or "quenching" of magma, is thus usually similar chemically to the magma from which it cooled. An obsidian flow is often remarkably homogeneous, and all pieces removed from it will have the same (or nearly) composition.

Elements present in rocks (including obsidian) in the highest concentrations (>1.0 % by weight) are referred to as "major" elements, and these include: O, Si, Al, Fe, Ca, Na, K, and Mg; although Ti, Mn, and P are not usually major elements, but minor, they are may be presented along with them. Elements present in lower concentrations (0.1-1.0 % by weight) are referred to as "minor" elements, and the particular elements that fall under this classification can vary. Elements present in the lowest concentrations (<0.1 %

by weight) are referred to as "trace" elements, and although these also can vary, the ones listed below are typically among them. Certain trace elements can be useful in petrology in determining the origin of rocks, and some of the most useful are the "transition metals" (Sc, Ti, V, Cr, Mn, Co, Ni, Cu, and Zn), the "lanthanides," or "rare earth elements" ("REE") (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), as well as Rb, Sr, Y, Zr, Nb, Cs, Ba, Hf, Ta, Pb, Th, and U.

A number of trace elements are also "incompatible" with the minerals often crystallizing in a cooling magma, and preferentially segregate to the liquid phase. As the fractionation of elements between solid and liquid phases proceeds during cooling and crystallization, incompatible trace elements (especially Th, U, Cs, Sr, Zr, Ti, and Rb, and the REE) become increasingly more concentrated in the remaining liquid. Despite their (usually) increasing concentration in the remaining magma over time, the ratios of incompatible trace elements to one another in this liquid often remain quite constant. It is hoped that continued study of incompatible trace element behavior may lead to a useful tool(s) for conducting obsidian provenance determinations (see Chapter 7).

Effects Due to Weathering

Obsidian, a natural glass formed due to the supercooling of lava, is unstable at Earth's surface conditions, and tends to weather quite rapidly; indeed, there are very few natural glasses older than ~100 million years (Bouška 1993). Inclusion of weathered portions may result in analyses that are not accurate representations of the fresh obsidian from which artifacts were typically fashioned. Bouška (1993) and Carmichael (1979) are good overall references for the following discussions. Natural glasses weather both physically and chemically. Physical weathering includes physical breakdown of larger pieces into smaller ones and structural breakdown of the glass itself (occurring along fractures, cracks, and other physical boundaries where water can gain access; also hydrous phenocrysts within the glass break down, releasing water). Chemical weathering occurs in 3 main ways: 1) hydration, wherein water becomes incorporated into the glass; 2) dissolution, wherein water becomes incorporated into the glass (hydration) and also extracts elements and/or ions from it; and, 3) devitrification, wherein the glass is converted to a crystalline state, resulting in its alteration to secondary minerals.

Hydration involves the capture of water to the glass surface, along with inter-diffusion of the water into the glass. If hydration continues undisturbed for some time, a sharp boundary (called a "rim") between the hydrated and non-hydrated layers will develop. Numerous factors affect the rate by which the hydration of obsidian proceeds; multitudinous studies have been undertaken to determine this rate, the various factors affecting the rate, and/or how long ago a piece of obsidian had been worked by man as based on the thickness of the hydration "rim" that has developed on it. Two fairly recent studies of this type are Anovitz et al. (1999) and Rogers (2006).

During dissolution, water both diffuses into the glass (hydration), and assists in diffusing main structural components such as Si and Al, and minor components such as Na, K, Ca, Mg, Li, Rb, and Cs, out of the glass. Of the trace elements, Ba, Li, Mn, Sr, and P are readily extracted, while Zn, Cu, As, Mo, Se, and U are difficult to extract. For a given glass, the rate of extraction is typically faster in acidic rather than alkaline medium. See also Friedman and Long (1984), Jezek and Noble (1978), MacDonald and Bailey (1973), Nickel (1987), Noble (1967), Piper (1994), and Zielinski et al. (1976).

Devitrification of glass results in the nucleation and growth of crystals within the relatively non-crystalline mass, and often results in conversion of the glass to felsite, perlite, pitchstone, rhyolite, or other crystalline phases, or the formation of "spherulites" (cryptocrystalline intergrowths of several minerals). Devitrification tends to result in loss of Na, U, F, and Cl from the original composition, an increase in Na in the crystallized areas and an increase of K in the residual glass. Devitrification tends to occur more quickly with elevated temperatures and addition of water. Hydrous phenocrysts within the glass can act as nucleation centers and tiny sources of water. See also Ewart (1971), Friedman and Long (1984), MacDonald and Bailey (1973), and Marshall (1961).

This author expects the most likely type of weathering the artifacts studied here experienced was hydration. The site descriptions and photographs (Lange 1995 ed., 1996 ed.) gave no evidence they were recovered from at or below the water table, thus unlikely they had been exposed to constant, or nearly constant, contact with water. Close contact with water would have resulted in a high rate of hydration, and to dissolution weathering given enough time. As the sites are no more than ~3500 years old (Lange 1996b, 1995), it is unlikely enough time elapsed for dissolution weathering to begin, even if enough water had been present. In addition, visual examination of the 96 obsidian debitage pieces (see Appendices A and C) revealed no signs any were undergoing crystalline transformation. Virtually all of the worked surfaces appeared vitreous, though 3 did have somewhat dullish surfaces (see Appendix C) which might be expected from hydration weathering (Bouška 1993; Piper 1994). According to Friedman and Smith's (1960) model for Ecuador (similar climate to Nicaragua), the calculated expected deepest depth of hydration weathering effects is ~6.20 μm (0.000620 cm) after 3500 years. Although numerous hydration rate models have been developed since their ground-breaking work, Friedman and Smith's (1960) model still serves as a good first approximation. A more exacting model was not thought necessary as this calculated depth was not deep when compared to the thickness of the 96 obsidian pieces (≥~0.5 cm). Therefore, the surfaces of the pieces were not expected to have undergone significant chemical alteration, and not removed prior to analysis (see Appendix A), with a high degree of confidence.

Ancient Use as Tool Material

Obsidian is a common artifact material, having been widely used by prehistoric peoples for the manufacture of tools, weapons, and other items. Obsidian exhibits three important qualities, the first two of which can be manipulated or controlled (to a large degree) to yield the desired end form, which is often the position(s), length(s), and direction(s) of the third: 1) it is brittle or "breakable," thus it can be "worked" by being fairly easily broken into large pieces, and knapped or chipped into smaller pieces; 2) it exhibits conchoidal fracture, thus fracture length and direction are not entirely pre-determined by the material itself (Jackson 1997); and, 3) its broken surfaces exhibit a sharp edge. Obsidian can be "worked" by knapping into many desired shapes and forms, as evidenced by the great variety of items that prehistoric man has left behind. Although natural glass can be found nearly anywhere a volcanic eruption has occurred, obtaining high-quality obsidian may have required travel, trade, or other means.

As noted, obsidian often contains numerous tiny crystals ("microlites") whose composition is dependent on the composition of the magma from which the obsidian formed (Best 2003; Bouška 1993; Hall 1996; Wilson 1989). The number and size of microlites in an obsidian will greatly affect its quality, with higher-quality obsidians containing fewer and smaller (Bouška 1993; Hughes and Smith 1993). The higher the quality of an obsidian, the more suited for knapping and shaping into tools, as it is easier for the craftsman to control the thickness, width, curvature, etc., of the resulting piece (for example: Andrefsky 2005; Healy et al. 1996; Hughes and Smith 1993; Yerkes and Kardulias 1993). Also affecting obsidian quality is the presence of tiny internal and/or external cracks, which may develop during initial lava cooling, or the initial stages of chemical weathering (Bouška 1993; Hughes and Smith 1993), or which may develop if subjected to fire or high temperature (see for example, Loyd et al. 2002).

The reader is referred to such references as Andrefsky (2005), Jackson and Love (1991), Kardulias and Yerkes (2003), Yerkes (2003), Yerkes and Kardulias (1993), as well as Lange (1996a), and Lange (ed. 1992 (see especially in that volume: Drolet 1992, Fowler 1992, Lange 1992a, 1992b, and 1992c, and Sheets 1992)), for information regarding the following. One of the most important characteristics of obsidian is its ability to form a sharp edge. Although it can be fairly easily knapped using another stone or piece of antler, special techniques and much practice may have been needed to produce more unique shapes, thus specialized craftsmen may have been dedicated to the craft; additionally, obtaining the greatest number of usable pieces from each "core" (largish chunks from which finished items were produced) may have come only with experience. Re-working and/or re-shaping of previously-used pieces of obsidian to produce either smaller versions of the same weapon or tool, or differently-shaped weapons or tools was not uncommon; pieces showing signs of re-working or re-shaping have been recovered from many archaeological sites. Obtaining obsidian of proper quality may have required travel, trade, or perhaps such extreme means as colonization, threats of force, warfare or conquest, as obsidian was an extremely important resource. Although obsidian can be abundant in some areas of the world, such areas were not necessarily habitable, or inhabited, by people. Thus, "ownership" of an obsidian source was likely greatly prized and well defended, and access to obsidian produced from that source (either as finished tools, weapons or other items, or as the "cores" from which items were produced) may have been limited, for a number of possible reasons.

CHAPTER 3

AREA OF STUDY

This study involves determining the chemical compositions for 100 artifacts (96 obsidian pieces, 2 other lithic pieces, and 2 pottery shards) excavated from 5 small archaeological sites in and near metropolitan Managua, Nicaragua, and ultimately determining the provenance for the 96 obsidian artifacts. In addition, 5 of the obsidian artifacts from 1 of these sites were discovered to have tiny copper droplets attached to their surface(s) (see Chapter 6). The provenance of the obsidian artifacts was determined via comparing their chemical compositions to those of known sources of obsidian in Central America and Mexico, using element versus element plots.

Archaeological Sites Included in This Study

Studied here are 100 artifacts of unknown composition (see Figures C-1 through C-10, Appendix C) excavated from 5 small archaeological sites located in and near metropolitan Managua, Nicaragua (see Figure 1). Dr. Frederick Lange, former Director of the Anthropological Museum at the University of Colorado at Boulder, Boulder, Colorado, USA, directed the 1996 Field Season excavations during which all 100 artifacts studied here were unearthed (Frederick Lange, verbal communication November 1999). These artifacts were selected from among the many excavated to serve as a representative sample in terms of both vertical and horizontal representation at the 5 different sites (Frederick Lange, written communication 8/10/2006). The ages of the sites range from possibly as old as 2000 BC to possibly as recent as 1520 AD, as determined by analysis of pottery and ceramics also found at the sites (Lange 1996b, 1995).

Excavations at these sites were performed as part of the Proyecto Arqueología de la Zona Metropolitana de Managua (or Archaeological Project of the Metropolitan Area of Managua) during the 1995 and 1996 Field Seasons (Lange 1996b, 1995). A main objective of the Proyecto Arqueología was to establish connections between concerned institutions for a long-term strategy of protection, conservation, and study of the area (Lange 1995). Although no further excavations have occurred in the metropolitan Managua area since the 1996 Field Season, work is on-going in the nearby Isthmus Rivas

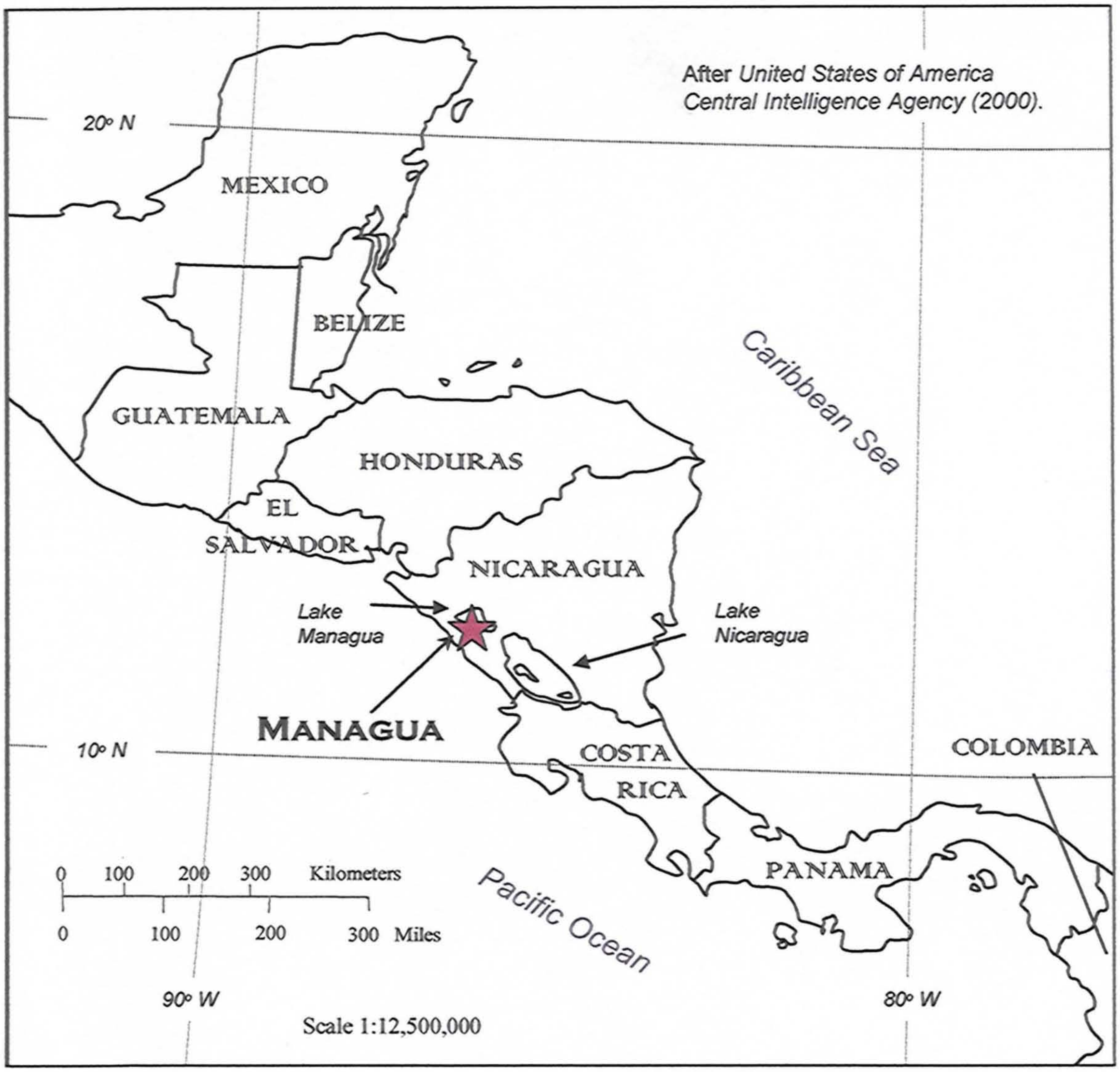


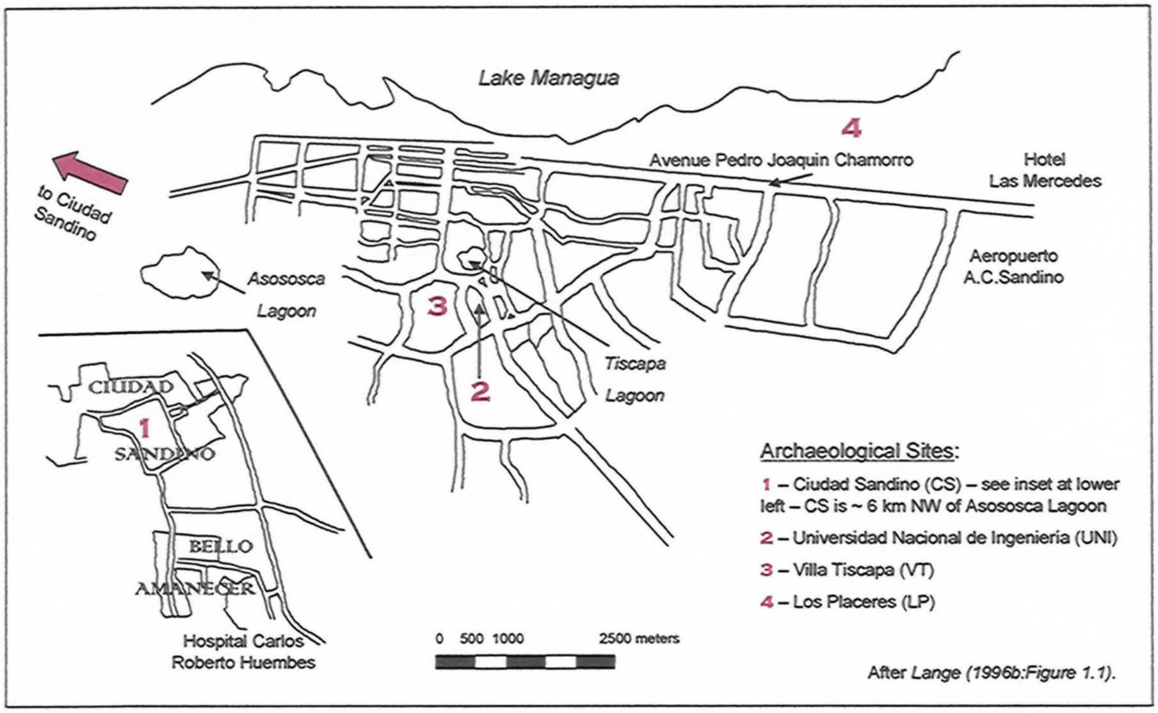
Figure 1. Map of Central America, showing the general location of the 5 archaeological sites studied here (in and near Managua, Nicaragua). (After United States of America Central Intelligence Agency [USA CIA] 2000.)

area (Frederick Lange, written communication 8/10/2006), the isthmian area between the Pacific Ocean and the western shoreline of Lake Nicaragua (Lange 1992b:Figure 1), ranging southeast of metropolitan Managua and continuing southeastward to the border between Nicaragua and Costa Rica (can be seen in Figure 3).

The 5 archaeological sites from which the artifacts studied here were excavated were quite small, and might be categorized as "test pits" (Frederick Lange, verbal communication November 1999). Four of these sites are located within metropolitan Managua, Nicaragua, along the southernmost shore of Lake Managua (or Lago Managua, or Lago Xolotlan): Ciudad Sandino (abbreviated here CS), Los Placeres (LP), Universidad Nacional de Ingeniería (or National Engineering University) (UNI), and Villa Tiscapa (VT) (Lange 1996b, 1995) (see Figure 2). The fifth is the Moyuá site (MO), consisting of excavations on 2 small islands, Isla Honda and Isla Seca (or Isla Moyuá), within Lake Moyuá (or Laguna de Moyuá), ~72 km (~45 miles) NNE of Managua (Lange 1996b) (see Figure 3).

Ciudad Sandino site (CS), N-MA-12 and N-MA-37

The Ciudad Sandino site (CS) consists of 2 excavations ~1 km apart (Frederick Lange, written communication 11/2/2000), within metropolitan Managua, Nicaragua (Figure 2); the site designations are N-MA-12 and N-MA-37 (Lange 1996b). Analysis of pottery and ceramics also recovered at the site (from the wider age range at N-MA-37) determined them to be possibly as old as 500 BC to possibly as recent as 1520 AD, which corresponds to the Tempisque (500 BC-300 AD), Bagaces (300-800 AD), Sapoá (800-1350 AD), and Ometepe Periods (1350-1520 AD) (Keller et al. 1996:85, 92). Site N-MA-12 consisted of a 2 m x 2 m test excavation to 3.6 m depth (González Rivas et al. 1996:79), while N-MA-37 consisted of 2 surveys, each 2 m x 2 m in area, with #1 to 85 cm deep and #2 to 125 cm (Keller et al. 1996:85-86). A total of 38 (all obsidian) of the 100 artifacts studied here (see Figures C-1 through C-4, Appendix C) were collected from the CS site (Keller et al. 1996:Figure 7.8 shows 8 of the 38 CS artifacts). As detailed elsewhere (Chapter 6 and Appendix C), five (all obsidian) of the 100 artifacts studied here were discovered to have tiny (<<1 mm to 1 mm) previously-molten copper droplets attached to their outer surface(s), with all 5 of these artifacts excavated from the CS site, 4 from N-MA-12 and 1 from N-MA-37 (Frederick Lange, written communication 11/2/2000). The depths from which these 5 artifacts were excavated ranged from 0-15 cm (N-MA-37) to 25-55 cm below the surface (N-MA-12), which corresponds to ~300-1200 AD (Frederick Lange, written communications 11/2/2000, 11/6/2000). No other



After *Lange (1996b:Figure 1.1).*

Figure 2. Map of metropolitan Managua, Nicaragua, indicating the locations of 4 of the 5 archaeological sites studied here. (After Lange 1996b:Figure 1.1.)

evidence of the working of molten metals have been discovered at the sites (Frederick Lange, written communication 11/6/2000).

Los Placeres site (LP), N-MA-1

The Los Placeres site (LP) consists of 2 "surveys" (test pits) and 2 "prospects" (surface collections) (Stauber 1996:49), within an ~100 m x 120 m area (Stauber 1996: Figure 4.2), within metropolitan Managua, Nicaragua (Figure 2); its designation is N-MA-1 (Lange 1996b). Analysis of pottery and ceramics also recovered determined them to be possibly as old as 300 AD to possibly as recent as 1520 AD, which corresponds to the Bagaces (300-800 AD), Sapoá (800-1350 AD), and Ometepe Periods (1350-1520 AD) (Stauber 1996:55). Survey 1 was 2 m x 2 m in area and 75 cm deep (Stauber

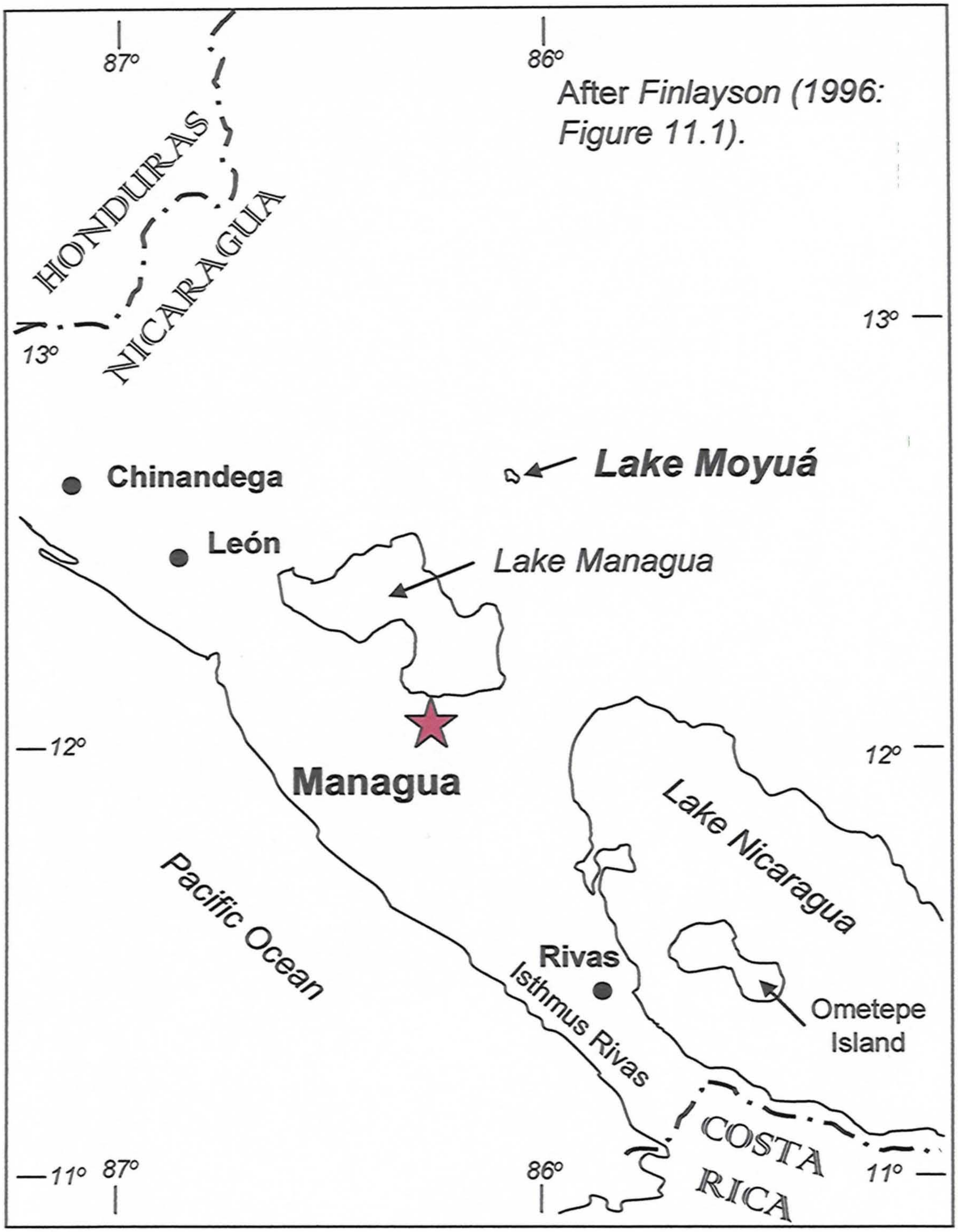


Figure 3. Map indicating the location of the Moyuá archaeological site in relation to the general location of the 4 other sites in metropolitan Managua, Nicaragua. (After Finlayson 1996:Figure 11.1.)

1996:56), Survey 2 was a total of 3 m x 2 m in area and 35 cm deep (Stauber 1996:59), and the surface prospects were 2 m x 2 m in area (Stauber 1996:52). A total of 5 (all obsidian) of the 100 artifacts studied here (see Figures C-4 and C-5, Appendix C) were collected from the LP site (Stauber 1996:Figure 4.4 shows all 5 LP artifacts).

Universidad Nacional de Ingeniería site (UNI), N-MA-62

The Universidad Nacional de Ingeniería (or National Engineering University) site (UNI) consists of 4 "Operations," sited on and adjacent to the UNI campus (Bargnesi et al. 1996:Figure 3.1) within metropolitan Managua, Nicaragua (Figure 2); the site designation is N-MA-62 (Lange 1996b). Analysis of pottery and ceramics also recovered determined them to be possibly as old as 2000 BC to possibly as recent as 1520 AD, corresponding to the Orosí (2000-500 BC), Tempisque (500 BC-300 AD), Bagaces (300-800 AD), Sapoá (800-1350 AD), and Ometepe Periods (1350-1520 AD) (Bargnesi et al. 1996:37, 44-45). The 4 Operations each consisted of a different number of surveys or excavations (Bargnesi et al. 1996:Figure 3.1): Operation #1 (an initial survey with 2 subsequent test excavations each 2 m x 2 m in area, up to 110 cm deep) excavated during the 1995 Season (Pichardo Pichardo and Zambrana Fernández 1995:77-79), and Operations #2-#4 (the deepest of which is 70 cm) excavated during the 1996 Season (Bargnesi et al. 1996:39), and each Survey being 1-2 m x 2 m in area (Bargnesi et al. 1996:Figure 3.3). A total of 8 of the 100 artifacts studied here (see Figures C-5 and C-6, Appendix C) were collected from the UNI site (Bargnesi et al. 1996:Figure 3.5 shows all 8 UNI artifacts), with these consisting of 4 obsidian pieces and all 4 non-obsidian pieces.

Villa Tiscapa site (VT), N-MA-36

The Villa Tiscapa site (VT) consists of 2 nearly adjacent excavations (Figure 2) within metropolitan Managua, Nicaragua; the site designation is N-MA-36 (Lange 1996b). Pottery and ceramics also recovered during the 1996 Field Season were determined to be possibly as old as 500 BC to possibly as recent as 1350 AD (Brown et al. 1996:10), although items from the 1995 Field Season suggest the dates may range from 2000 BC to 1520 AD (Lange 1995:4-6; Pullen 1995); the wider range corresponds to the Orosí (2000-500 BC), Tempisque (500 BC-300 AD), Bagaces (300-800 AD), Sapoá (800-1350 AD), and Ometepe Periods (1350-1520 AD) (Brown et al. 1996:10; Lange 1995:6). A fire-pit discovered in the 1996 excavation, 40 cm below the surface, was carbon-dated to ~70 AD ± 40 years (Brown et al. 1996:31). The 1995 site visit was an initial surficial survey, later enlarged to 4 m x 4 m and 2.6 m deep (Lange 1995:5-6); the 1996 visit was a 6 m x 6 m excavation, 80 cm deep, 1 m from the first (Brown et al. 1996:10, 22, 23, 27). A total of 44 (all obsidian) of the 100 artifacts studied here (see Figures C-6 through C-10, Appendix C) were collected from the VT site (Brown et al. 1996:Figures 2.8 and 2.9 show 18 of the 44 VT artifacts).

Moyuá site (MO)

The Moyuá site (MO) consists of excavations on 2 small islands, Isla Honda and Isla Seca (or Isla Moyuá), in Lake Moyuá, roughly 72 km (~45 miles) NNE of Managua, Nicaragua (Finlayson 1996) (Figure 3). Pottery and ceramics also recovered were determined to be possibly as old as 500 AD to possibly as recent as 1520 AD (Finlayson 1996:135, 145), corresponding to the Bagaces (300-800 AD), Sapoá (800-1350 AD), and Ometepe Periods (1350-1520 AD) (Finlayson 1996:135). The excavation on Isla Honda consisted of 14 transects (surficial collections) each ~20 m long (Finlayson 1996:135); Isla Seca had one 1 m x 1 m excavation 40 cm deep (Finlayson 1996:135). A total of 5 (all obsidian) of the 100 artifacts studied here (Figure C-6, Appendix C) were collected from the Moyuá site (Finlayson 1996:Figure 11.2 shows all 5 Moyuá artifacts).

Artifacts Included in This Study

One hundred artifacts of unknown composition were studied here (see Figures C-1 through C-10, Appendix C), consisting of 96 obsidian pieces, 2 other lithic pieces, and 2 pottery shards. Although all 96 obsidian pieces and both other lithic pieces fall into the category of "debitage," a catch-all term used by archaeologists for unwanted or unusable pieces or chips left over from the manufacture of blades, points, scrapers, and other tools, thus are "artifacts" in the most general sense of the term in that they have been generated by man (Frederick Lange, verbal communication November 1999). All 98 pieces of lithic debitage studied here had varying amounts of surface wear, shaping (by knapping or chipping), and unworked surfaces. More archaeologically-oriented characteristics, such as type and style of tool, style of manufacturing, etc., are beyond the scope of this study; some of these data are found in Lange (ed. 1995, ed. 1996), and other data are intended for future publication (Frederick Lange, verbal communication November 1999). In addition to the information below, 5 of the 96 obsidian artifacts were observed to have tiny copper droplets attached to their outer surface(s) (see Chapter 6).

Obsidian Artifacts

The 96 obsidian debitage pieces were of various sizes, shapes and masses, and had a small range of colors. See Appendix C for photographs (Figures C-1 through C-10) and more complete descriptions. The mass (and size) of the obsidian pieces ranged from the smallest at 0.0821 g (~1 x 1 x 0.1 cm, VT-36), to the largest at 17.9730 g (~3.5 x 3 x 3.5 cm, MO-03). The shape of most ranged from irregular chunks to irregular chips, although 2 may be broken portions of arrowheads, and perhaps as many as 16 may be broken portions of prismatic (elongate) blades. The color of the obsidian did not vary greatly, from the darkest, "black," Munsell designation "N1," to the lightest, "grayish black," N2 (Geological Society of America [GSA]1995). The amount of "working" is seen in the amount of fresh obsidian on the surfaces, and this ranged from 0% (just 1 piece), to 100% (30 pieces), with the majority of pieces (65) having some amount in-between. All unworked surfaces on the obsidian debitage pieces appeared to consist of what likely are remnants of original cooling "crust" surfaces (see Chapter 2), except dullish surfaces on 3 of them, with these appearing to be due to light weathering (see Appendix C, Artifact Descriptions section).

Artifacts of Other Composition

These 4 artifacts were comprised of 2 non-obsidian lithic materials (a quartz pebble and a broken blade of silicified conglomerate), and 2 shards of different types of pottery. See Appendix C for a photograph (Figure C-5) of both other lithic debitage pieces and more complete descriptions of them. The quartz pebble was fairly small (~3.25 x 1.5 x 1.5 cm, 1.0046 g), teardrop-shaped, and composed of massive quartz. Its color ranged from "very pale orange," 10 YR 8/2, to "pale grayish orange," 10 YR 8/4 (GSA 1995); there was some iron staining on this piece, which ranged from "dark yellowish orange," 10 YR 6/6, to "dusky yellowish brown," 10 YR 2/2 (GSA 1995). Although no signs of wear were observed on this piece at 40x magnification, the excavation report referred to it as a "quartz drill point" (Bargnesi et al. 1996:Figure 3.5; see Appendix C). The silicified conglomerate piece was a moderately-sized (~7 x 3 x 0.35 cm, 1.5441 g), thin, elongate blade, which had been broken diagonally along its longest dimension. Its overall color was "pale grayish orange," 10 YR 7.5/3 (GSA 1995), although iron staining on the piece ranged from "moderate brown," 5 YR 4/4, to "dark yellowish brown," 10 YR 4/2 (GSA 1995). It was composed of matrix-supported (~50% matrix) conglomeratic fragments of various colors and sizes, ranging from sub-angular to rounded. Some wear was observed on the edges of the piece (at 40x), suggesting use prior to burial; in addition, the entire surface, including the diagonally-broken surface, had a dullish appearance and feel, likely resulting from some amount of weathering.

The final 2 artifacts consisted of unglazed, unpainted, unslipped, wedge-shaped pottery shards of a light density. Each was of a different color, and had different designs incised or impressed into just one surface. See Appendix C for photographs (Figures C-5 and C-6) and more complete descriptions. The first piece was moderately-sized (~4 x 2.5 x 0.25 cm, 0.7860 g), and "moderate grayish brown" in color, 5 YR 3/3 (GSA 1995). The surface into which a design had been incised or impressed was convex in shape, thus likely the outer surface of this shard (Anderson 1985; Rice 1987). A small amount of ground-in soil could not be removed from its surfaces, as it was quite soft and easily scratched; such softness is indicative of unfired pottery (Anderson 1985; Rice 1987). The second piece was also moderately-sized (~4 x 3.75 x 0.25 cm, 0.4556 g), though "grayish black," N2.5 (GSA 1995). The surface into which a design had been incised or impressed was concave, thus likely an inner surface (Anderson 1985; Rice 1987). Nearly all ground-in soil was removed from this piece, as it was harder than the first; this higher hardness is indicative fired pottery (Anderson 1985; Rice 1987).

Potential Obsidian Sources

There are numerous "known" (identified, with locations known and samples collected and analyzed) sources of obsidian in Central America, Mexico, South America, and North America, and any of these obsidians may, theoretically, have served as source material(s) from which any (or all) of the 96 obsidian debitage pieces studied here were produced, as these land masses are all joined together. Trade or movement of obsidian over long distances, especially overland, is not unknown, and is addressed below briefly. Therefore, during the course of this study perhaps all obsidian sources in these areas need be seriously considered to determine the provenance for all 96 debitage pieces. All these obsidian sources are discussed in their rough order of geographical distance from the archaeological sites (closest to farthest), approximating the likelihood of their utilization at the sites. There may be a number of reasons a more distant source might have been utilized rather than a closer one, however (see Chapter 2 for some such reasons).

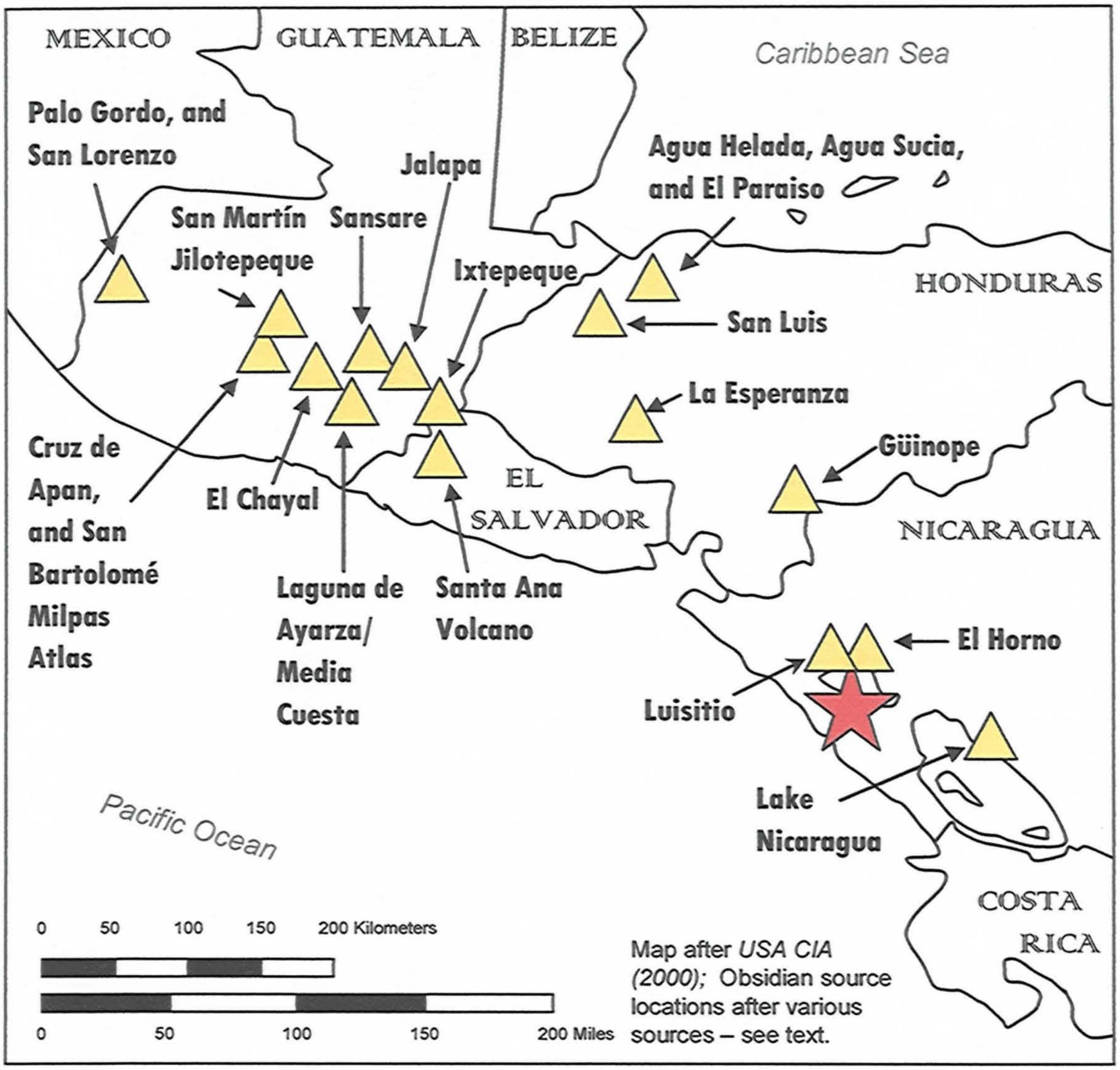
A prodigious number of studies have addressed the possible (maximum) length(s) of ancient obsidian trade routes (see for example, Moholy-Nagy 2003, a summary of many studies focusing on Mexico and Central America). Often, resulting interpreted exchange or movement systems are termed "long-distance," although length is apparently not the emphasis for this term: "Long-distance exchange is viewed as a special situation in which the materials exchanged crossed obvious boundaries: geographic, social, or political" (Glascock 2002:vii). Muddling the issue of trade route length is the extreme size of some obsidian sources, with vast areal extents over which "outcrops" (solidified flows and/or secondarily-distributed pieces) have been identified. For example: El Chayal, Guatemala, with flows identified over >100 km^2 (>~40 mi^2) in area (Cobean et al. 1991:76); San Martín Jilotepeque, Guatemala, with flows (and several secondarily-deposited "river cobbles") over >120 km^2 (>~45 mi^2) in area (Glascock et al. 1998:Figure 2.4, 40); Ixtepeque, Guatemala, with flows identified up to 300 km^2 (>~120 mi^2) in area (Cobean et al. 1991:77); Pachuca, Hidalgo, Mexico, with flows identified over >300 km^2 (>~120 mi^2) in area (Cobean et al. 1991:74). Additionally, obsidian nodules found in washes or alluvium have been geochemically identified to have originated as far away as 250 km (~155 miles) (Shackley 2002:56).

It is not uncommon for artifacts derived from Mexican obsidian sources to be unearthed in Guatemalan, Belizean, and Honduran archaeological sites, and similarly, for Guatemalan and Honduran obsidians to be represented in Mexican and Belizean archaeological sites (see Moholy-Nagy 2003, a summary of many studies). The longest distances this researcher has encountered in the literature for the movement of obsidian are regarding this area of the world: ~1100 km (~685 miles), between the Central Peten Lakes, Guatemala, archaeological site, and the Zacuáltipan, Hidalgo, Mexico, obsidian source (Moholy-Nagy 2003); and, ~1200 km (~750 miles), between the Chichén Itzá, Yucatán, Mexico, archaeological site and the Ucareo, Michoacán, Mexico, obsidian source (Braswell and Glascock 2002:38). The most extreme example encountered is for an artifact from the Spiro Mounds archaeological site (~850-1450 AD) in eastern Oklahoma, recently determined to have originated from the Pachuca, Hidalgo, Mexico, obsidian source, a distance of ~1800 km (~1120 miles) overland (Barker et al. 2002).

Central American Obsidian Sources

There are 20 "known" sources of obsidian in Central America, whose locations are identified and for which specimens have been collected and analyzed: 2 in Nicaragua (Sheets et al. 1990; Stross et al. 1992), 6 in Honduras (Aoyama et al. 1999; International Association for Obsidian Studies [IAOS] 2007), 1 in El Salvador (Stross et al. 1976), and 11 in Guatemala (IAOS 2007; Nelson et al. 1983). In addition, there is 1 "prospective" obsidian source in Nicaragua, for which no known specimens exist (Sheets et al. 1990; Stross et al. 1992). See Figure 4 for locations of these 21 sources, and Appendix D for a discussion and summary of the chemical data (in Table D-1) utilized here for those sources with such data (20 out of the 21 sources).

Nicaragua. Of the numerous volcanoes in Nicaragua, most are of basaltic composition, although several have compositions ranging from highly mafic (basaltic) to highly silicic (rhyolitic) (Carr et al. 2007; van Wyk de Vries et al. 2007; Weyl 1980). Therefore, most volcanic glass that may be found in Nicaragua would likely be of basaltic composition, and thus also would most likely not be of sufficient thickness or quality for producing tools or weapons (see Chapter 2). The 3 obsidian sources (2 known, 1 prospective) located in Nicaragua (see Figure 4) consist of what are likely deposits of stream cobbles of varying size, quality, and composition, and of unknown areal size and extent. The first consists of 3 "pebbles" collected from a stream cut near the town of Luisitio ("Luisitio," abbreviated here LU), west of Lake Managua, and the second consists of 2 "nodules" collected from the northeastern shore of Lake Nicaragua



Map after *USA CIA (2000);* Obsidian source locations after various sources – see text.

Figure 4. Map indicating the locations of all 21 known and prospective obsidian sources in Central America in relation to the general location of the 5 archaeological sites studied here (in and near Managua, Nicaragua). (Map after USA CIA 2000; Obsidian source locations from numerous sources, listed in text.)

("Lake Nicaragua," LN),~20 km northeast of the town of Juigalpa (Sheets et al. 1990:150, 153; Stross et al. 1992:131), ~60 and ~90 km (~40 and ~55 miles) respectively, from the 5 archaeological sites studied here. The third consists of small (<1 to 6 cm) “nodules” observed in a road cut near El Horno (referred to here as the “El Horno” source, EH), ~40 km north of Lake Managua (Sheets et al. 1990:153; Stross et al. 1992:131-133), ~65 km (~42 miles) from the archaeological sites; no known specimens were collected from this “source,” and no chemical analyses for such have been identified in the literature. Owing to the small sizes of all known and observed pieces for all 3 of these obsidian “sources,” none are believed to have been able to yield blades or other tools (Sheets et al. 1990:153), thus are not seriously thought to be sources of archaeological obsidian, unless further visits reveal more evidence (Sheets et al. 1990:153; Stross et al. 1992:133). To be thorough, however, the available chemical data for LU and LN (see Table D-1, Appendix D) were compared against the chemical data for the 96 obsidian debitage pieces studied here (see Chapter 5 and Appendix D).

Honduras. There are a limited number of volcanoes in Honduras, about evenly divided between basaltic and rhyolitic composition (Carr et al. 2007; van Wyk de Vries et al. 2007; Weyl 1980), thus it is likely that Honduran volcanic glasses would reveal a wide compositional variation. The distance from the 6 known obsidian sources in Honduras (Agua Helada (AH), Agua Sucia (AS), El Paraiso (EP), Güinope (GUIN), La Esperanza (ESP), and San Luis (SLU)) to the archaeological sites studied here range ~180-390 km (~115-245 miles) (Aoyama et al. 1999; IAOS 2007); see Figure 4. Of these, GUIN (closest, at ~180 km or ~115 miles) and ESP (2nd closest, at ~315 km or ~195 miles) have most often been determined to be source materials for artifacts uncovered from various Central American archaeological sites (for example: Glascock et al. 1991; Healy et al. 1996; Sheets et al. 1990; Stross et al. 1992), and thus particularly important to include here. For thoroughness, however, chemical data for all 6 known Honduran sources (see Table D-1, Appendix D) were compared to the chemical data for all 96 obsidian debitage pieces (see Chapter 5 and Appendix D).

Costa Rica, El Salvador, and Panama. Both Costa Rica and El Salvador contain numerous volcanoes, mostly of basaltic composition, although a number range into more silicic compositions (up to andesitic) (Carr et al. 2007; van Wyk de Vries et al. 2007; Weyl 1980). Panama, however, contains fewer volcanoes, with compositions ranging from basaltic to rhyolitic (about half each) (Carr et al. 2007; van Wyk de Vries et al. 2007; Weyl 1980). Most volcanic glass formed in Costa Rica or El Salvador would likely also be of basaltic composition, and thus also probably not of sufficient thickness or quality for producing tools or weapons (see Chapter 2). Indeed, Lange (1996a:316) states that no "obsidian" has been found in Costa Rica "in usable size or quality [of] nodules or veins," although his (and other archaeologists') use of the term "obsidian" may be less exacting with regard to composition than that strictly implied by usage of the term. No mention has been found for any obsidian source in El Salvador or Panama either, save a single analysis for "obsidian" from the Santa Ana Volcano (SAV), El Salvador (Stross et al. 1976:248), ~420 km (~260 miles) from the archaeological sites (see Figure 4). The chemical data for this sample (see Table D-1, Appendix D) was compared to the chemical data for all 96 obsidian debitage pieces (see Chapter 5 and Appendix D). Although archaeological sites in both Costa Rica and El Salvador contain evidence of obsidian tool manufacture on-site (such as cores and debitage; see for example: Sharer 1984; Sheets 1984, 1992), the sources for all such obsidian pieces and debitage have been chemically determined to be located in Guatemala, Honduras, and Mexico (for example: Sharer 1984; Sheets 1984).

Guatemala. There are numerous volcanoes in Guatemala, and although most are of basaltic composition, a significant number are rhyolitic (Carr et al. 2007; van Wyk de Vries et al. 2007; Weyl 1980), thus volcanic glass formed here likely reveals a correspondingly wide compositional variation. The distance from the 11 known Guatemalan obsidian sources (Cruz de Apan (CDA), El Chayal (EC), Ixtepeque (IXT), Jalapa (JAL), Laguna de Ayarza (LDA), Media Cuesta (MC), Palo Gordo (PG), San Bartolomé Milpas Atlas (SBMA), San Lorenzo (SL), San Martín Jilotepeque (SMJ), and Sansare (SNS)) to the archaeological sites range ~435-690 km (~270-430 miles) (IAOS 2007; Nelson et al. 1983); see Figure 4. Of these, IXT (closest, at ~435 km or ~270 miles), EC (~555 km or ~345 miles), and SMJ (~570 km or ~355 miles) have most often been determined to be source materials for Central American obsidian artifacts (for example: Brown et al. 2004; Glascock et al. 1991; Sheets et al. 1990), thus were of particular importance to include here. Although, for thoroughness, chemical data for all

11 Guatemalan sources (see Table D-1, Appendix D) were compared to that for all 96 obsidian debitage pieces (see Chapter 5 and Appendix D).

Mexican Obsidian Sources

Mexico contains an abundant number of volcanoes, of varying composition from basaltic to rhyolitic (for example: Best 2003; Hall 1996; Wilson 1989; Winter 2001), thus volcanic glass compositions would likely vary as widely. There are at least 66 known obsidian sources in Mexico (listed alphabetically by State): Baja (4), Chihuahua (5), Durango (2), Guanajuato (1), Guerrero (1), Hidalgo (7), Jalisco (17), Michoacán (6), Nayarit (2), Puebla (4), Querétaro (8), Sonora (2), Mexico (1), Veracruz (4), and Zacatecas (2) (Cobean et al. 1971; Ericson and Kimberlin 1977; Glascock et al. 1988; Harris 1986; IAOS 2007; Stross et al. 1976; Zeitlin and Heimbuch 1978). These sources range as close to the archaeological sites studied here as the middle of the State of Veracruz (Pico de Orizaba source), ~1600 km (~1000 miles), to as far as northern Sonora (Los Vidrios source), ~3600 km (~2250 miles) (Cobean et al. 1971; Ericson and Kimberlin 1977; Glascock et al. 1988; Harris 1986; IAOS 2007; Stross et al. 1976; Zeitlin and Heimbuch 1978). As all 66 are quite some distance from the sites, it is unlikely any are sources for any of the artifacts studied here. Review of the published literature (from 1976 onward) revealed that 11 of these 66 (in approximate order from closest to the sites to farthest: Pico de Orizaba and Altotonga (both in the State of Veracruz), Guadalupe Victoria, Paredón, and Zaragoza (Puebla), Zacuáltipan, Tulancingo, and Pachuca (Hidalgo), Otumba (Mexico), Zinapécuaro and Ucareo (Michoacán)) had most often been determined to be the source materials for Central American obsidian artifacts (see as an example: Moholy-Nagy 2003). Therefore, chemical data for these 11 sources (see Table D-1, Appendix D) were compared to that of the 96 obsidian debitage pieces, as 1 piece had remained without provenance after comparison with the Central American sources (see Chapter 5 and Appendix D). None of the 66 Mexican obsidian source locations are shown here, as only 1 (1 of the 11 selected) was determined to potentially have been the source material for just the 1 obsidian debitage piece.

South American Obsidian Sources

There are a multitude of volcanoes throughout the South American continent, especially in the countries of (from north to south): Colombia, Ecuador, Peru, Bolivia, Chile, and Argentina (for example: Best 2003; Hall 1996; Wilson 1989; Winter 2001). There are at least 41 known obsidian sources in South America (listed alphabetically by country): Argentina (16); Bolivia (3), Chile (2), Colombia (3), Ecuador (3), and Peru (14) (Barnes et al. 1970; IAOS 2007). These sources range in distance to the archaeological sites from as near as the Rio Hondo source in the western portion of Colombia, ~1700 km (~1060 miles), to as far as the Seno Otway source near the southern tip of Chile, -7700 km (~4800 miles) (Barnes et al. 1970; IAOS 2007). Because all 41 are such considerable distances from the archaeological sites, none were included in the comparisons performed here (nor are locations shown), as the likelihood of any being source material for the debitage pieces was very low. The results obtained here reveal that elimination of these sources likely is correct (see Chapter 5 and Appendix D).

North American Obsidian Sources

The upper portions of the North American continent contains a vast number of volcanoes, especially throughout the western portion of the contiguous United States of America (USA), and along westernmost Canada and southern Alaska (for example: Best 2003; Hall 1996; Wilson 1989; Winter 2001). There are at least 379 total known sources of obsidian in these areas: 352 in the contiguous USA, 17 in Canada, and 10 in Alaska (IAOS 2007). These sources are located at even more extreme distances from the archaeological sites, with the nearest being the Rio Grande Gravels source in southwest Texas, ~3150 km (~1960 miles), and the farthest the Batza Tena source in west central Alaska , ~8250 km (~5150 miles) (IAOS 2007). Due to such extreme distances, these obsidian sources were believed even less likely source materials for any of the debitage pieces, and were not considered further (and locations not shown). Just as with the South American obsidian sources, elimination of the North American sources likely is correct (see Chapter 5 and Appendix D).

CHAPTER 4
METHODOLOGY

One hundred artifacts (consisting of debitage: 96 obsidian pieces, 2 other lithic pieces, and 2 pottery shards) excavated from 5 small archaeological sites in and near metropolitan Managua, Nicaragua, were studied here. The methodology entailed 2 main phases: 1) determination of chemical compositions for all 100 artifacts; and ultimately, 2) determination of provenance (origin of materials) for the 96 obsidian debitage pieces. The provenance determinations performed here used mainly trace elements to compare the pieces to potential sources. Central American obsidians were the main focus during the comparison, as closer materials are more likely to have been sources, and Mexican obsidians were a secondary focus; no further sources were compared, as the pieces are believed to be provenanced as completely as possible (see Chapter 5 and Appendix D).

Analytical Methodology

The analytical methodology followed here consisted of two main steps: 1) observation of the physical characteristics of all 100 artifacts; and, 2) determination of the chemical composition of all 100 artifacts (all of unknown composition). Although summarized below, more details are given in Appendices A and C.

Physical Characteristics of the Artifacts

The 100 artifacts studied here were observed visually prior to their preparation for chemical analysis; this information is presented briefly in Chapter 3, and in more detail in Appendix C. There were 2 objectives for visual study of the artifacts: 1) identification of any resistant phases; and, 2) identification of any discernable physical structures, or unique minerals, within the 96 obsidian pieces. Resistant minerals can be difficult to break down, thus identification of such phases can be critical for obtaining accurate chemical analyses. Unique minerals or structures within an obsidian piece may allow for more complete characterization of the obsidian from which it was formed. These visual studies were performed at up to 40x magnification using a plane light binocular microscope (housed in the Chemistry and Geochemistry Department, CSM), up to 800x magnification using a plane and cross-polarizing light binocular microscope (housed in the Geology and Geological Engineering Department, CSM), and a 10x hand lens owned by this researcher. A number of copper droplets were discovered attached to 5 obsidian debitage pieces; 2 droplets were removed from 1 piece, thin sections prepared of these and also observed (see Chapter 6 for information regarding the copper droplets).

Chemical Compositions of the Artifacts

Chemical analysis of the 100 artifacts was obtained via an Inductively-Coupled Plasma Mass Spectrometer (ICP-MS), which was housed at the United States Geological Survey (USGS), Lakewood, Colorado, USA, and operated by Allen Meier, Research Chemist with the Crustal Imaging and Characterization Team, Geologic Division, Department of the Interior, USGS. More detailed information regarding preparation of the artifacts for analysis, the analytical runs of this study, and other related information, can be found in Appendices A and B. The analytical data obtained here for all 100 artifacts is presented in Table C-1, Appendix C.

Obsidian Provenance Sourcing Methodology

Studies sourcing obsidian artifacts back to their materials of origin using chemical data have been published in seemingly ever-increasing numbers since the 1960's (see for example: Cann and Renfrew 1964; Heizer et al. 1965; Weaver and Stross 1965). This abundance of chemical studies is both a "blessing" and a "curse." It is a "blessing" in that 1) the source materials for an ever-increasing number of obsidian artifacts have been identified, allowing for delineation of ancient trade routes and settlement patterns (for example: Jackson and Love 1991; Negash and Shackley 2006), and patterns of use over time for source materials (for example: Brown et al. 2004; Jackson and Love 1991), etc.; and, 2) numerous obsidian sources have been identified by their unique chemistry first, with their physical existence later confirmed as outcrops or deposits are found in likely area(s) and analyzed. For example, Shackley (2005:97) states that most of the over 40 known obsidian sources in Arizona, New Mexico, northern Sonora and northern Chihuahua were "investigated or discovered as a result of detecting a number of 'unknown' sources in archaeological contexts." As chemical data for artifacts are statistically analyzed, they are scrutinized regarding clustering (Glascock 1994:118-119; Glascock et al. 1998:24-32). If any new clusters are significantly different from other clusters, and do not aggregate with any known obsidian sources, they are thus from as yet unknown or unidentified sources (Glascock et al. 1998:24-32). Such was the case with 2 groups of artifacts from La Entrada, Honduras, studied by Glascock et al. (1991). The source obsidian for 1 of these groups was later determined by Aoyama et al. (1999) to be the newly identified San Luis, Honduras, source, and 1group still remains unknown. If an "unknown" cluster is similar in composition to other "known" clusters in an area, then it is likely close in geographical context and can be located (Shackley 2005:97).

However, it is also a "curse": 1) the ambiguity or uncertainty of assigning an artifact to a particular source based solely on compositional range at times also increased, as instances were encountered in which obsidian sources with similar composition were being compared; both Asaro et al. (1978: 436) and Zeitlin and Heimbuch (1978:123) point out this potential problem, and an earlier group (Stross et al. 1976) seem to hint at it also. And, 2) the complexity of statistical approaches or methods that researchers have developed for delineating between sources and/or determining assignments of artifacts to sources has also increased (see as examples: Braswell and Glascock 1998; Glascock et al. 1988; Glascock et al. 1998), and understanding the exact steps undertaken to repeat the results attained thereby may be problematic. It is exactly this situation that Michels (1982) encountered, in attaining only 58% source assignment certainty when attempting to reproduce the source assignments determined by another group (Hurtado de Mendoza and Jester 1978). Repeatability is at the heart of the scientific method, and necessitates methodology that produces the same results each time. The search to fill this need for reproducibility of results as well as for a standardized, or more than is the state now, method of performing geochemical obsidian provenance studies that has been a secondary, although important, factor in a number of more recent studies, and a number of possible recommendations toward such achieving goals are made here in Chapter 7.

Sourcing Methods Used in Previous Studies

The methods used in sourcing obsidian artifacts to their materials of origin are numerous, and in addition to chemical, include: visual, density, refractive index, magnetic susceptibility, thermoluminescence, fission track, and weathering depth profiles. Although some studies involving these other parameters (other than chemical) have yielded significant and/or interesting results (for example: Braswell (1996:479-482) found he had both chemically and visually assigned the same artifacts to the same sources; and, Bellot-Gurlet et al. (1999) using a combination of chemical data and fission track age-dating obtained interesting results, although they insist artifacts of extremely similar composition but yielding different fission track ages absolutely must have come from different obsidian sources), all of these other parameters tend to vary widely, even within a single obsidian flow. Thus, using these parameters may yield good results for more well-defined studies in which determinations are being made between two or more sources with very different, and well-constrained, values. As Moholy-Nagy and Nelson (1990) (with disappointing 53.3% correct results for visual sourcing) noted, knowing the visual parameters of obsidian sources may, in time, assist in excluding certain ones from a given sourcing study. Using chemical data in an exclusionary manner, to exclude certain sources from further consideration as source materials for certain obsidian artifact(s), has been used during nearly every obsidian chemical sourcing study that has been conducted since the late 1960's, when enough sources were known and considered in a given study, and may become an even more powerful tool for obsidian sourcing studies in the future (see Chapter 7).

As interesting as these other parameters (other than chemical) are for conducting obsidian sourcing studies, they have often yielded mixed results. The main type of obsidian sourcing study has been chemical, as such results have been the most reliable and reproducible. However, the specific elements utilized in the sourcing determinations have appeared to be based upon a wide variety of factors, including: the methodology and/or instrumentation used (what was available or familiar, or what may have been desired to be tested by the researcher, such as a new instrument or methodology), what is usually (or not usually) tested for, what has been useful in previous studies, what has been useful for that particular source(s) or area of the world, and perhaps what may have been the preference of the researcher and/or institution. Thus, the particular elements analyzed have varied from study to study, with continuity of such varying widely between studies except those conducted usually by the same researchers and/or at the same institutions. Numerous pleas have been made over time for standardization of some type (usually for elements presented, but also for units presented or plot types presented) (for example: Moholy-Nagy 2003; Stross et al. 1976).

Previous studies have utilized any number of elements for chemical sourcing of obsidian artifacts, with the fewest being 2 elements (using Na and Mn: Gordus et al. 1967) and 3 elements (for example, using Rb, Sr, and Zr: Hester et al. 1973; Jack and Heizer 1968), although these tend to be older studies, with newer ones usually presenting more complete chemical compositions for both artifacts, and sources, if data is presented at all. In some studies, an initial chemical analysis has been performed using fewer elements than usual, after which sourcing of some of the artifacts was determined, and then another, more detailed chemical analysis was performed, and the remaining artifacts sourced (for example: Glascock et al. 1994; Stross et al. 1983). However, these particular studies were usually investigations into the effectiveness of somewhat altered, or "abbreviated," methodologies of the same methods usually used, as finding less-costly, less time-consuming, and less-destructive methods of sourcing are of much interest to archaeologists (Glascock et al. 1994:29). A method used for analyzing materials non-destructively, photon activation analysis, has very recently been applied to obsidian artifacts from archaeological sites in the Aleutian Islands, Alaska, for determining their provenance (Associated Press 2007). Unfortunately, many studies, including recent ones, fail to indicate exactly which elements were used to accomplish the sourcing determinations they present. A number of elements have been used to successfully source obsidian artifacts, including major elements (such as Na and Fe) and minor elements (such as Ba, Mn, and Ti), although trace elements (such as Ce, Cs, La, Nb, Rb, Sr, Th, U, and Zr) have been the most successful and reliable for sourcing studies, thus have been used increasingly and are now often the foundation of current obsidian geochemical sourcing studies.

Current Methodologies for Obsidian Sourcing Studies

The actual techniques or methodologies by which the source assignments have been determined in previous chemical studies have varied somewhat, although the main approach by which all have been performed is that of comparing the compositions of artifacts to those of likely source materials, these typically being located near where the artifacts were excavated. There are two different, though related, main methods currently used for conducting obsidian geochemical sourcing studies: 1) comparing compositional data for artifacts to the compositional data range (minimum through maximum) for sources for a number of elements; those artifacts whose compositions fall within the compositional range (+/- some amount of deviation) for a given source, or extremely close thereto (usually within that amount of deviation, or very close to), are thus "assigned" to it (for example: Stross et al. 1983). A variation of this method uses elemental ratios, with these being compared in a similar manner (for example: using Fe/Mn ratios: Brown et al. 2004; using Rb:Sr:Zr and Fe:Mn ratios: Jackson and Love 1991:50; using Rb/Zr and Sr/Zr ratios: Andrews et al. 1989; Fowler et al. 1989; Healy et al. 1984; McKillop et al. 1988; Moholy-Nagy et al. 1984; Sheets et al. 1990; Stross et al. 1983; using Ce/Ba, Rb/Zr, Sr/Zr, Nb/Zr, and Y/Zr ratios: Rice et al. 1985); however, all of these named studies used X-Ray Fluorescence (XRF) for measuring compositions, and these particular ratios may have been "artifacts" of the instrumental methodology, and serendipitously turned out to be useful for distinguishing between sources. And, 2) plotting (element versus element plots for a number of elements) artifact sample data against source sample data, and those artifact samples falling clearly within the "envelope" as defined by the sample population (again, +/- some amount of deviation) for a given source, or extremely close thereto (again, usually within that amount of deviation, or very close to), thus "assigned" to it (for example: Brown et al. 2004; Dahl et al. 1990). This second method is the one utilized here, as discussed in the next section, Chapter 5, and Appendix D. With both of these main methods, if any artifact sample(s) falls significantly outside the source sample ranges or "envelopes," then more sources are included and the process repeated. If no other sources are known for the area, then that artifact(s) may have been fashioned from an obsidian source(s) not yet identified in that area, or the situation may be more complex, with longer-distance movement of materials than had been previously considered.

A main drawback to these two methods is that of implied and/or real ambiguity of sourcing determinations. As mentioned earlier, instances have occurred in which two or more obsidian sources with similar chemical compositions have been compared, thus the ranges of compositions or plotted data points for these sample populations overlap or merge for some, possibly even most, elements. For example, the El Chayal, Guatemala, and Güinope, Honduras, obsidian sources, ~400 km (~250 miles) apart, have extremely similar chemical compositions, and are both included in this study (see Chapters 3 and 5, and Appendix D). To have the clearest, least ambiguous sourcing results, the source sample populations need to be clearly differentiated or separated from one another. Otherwise, if two or more sources overlap for a number of elements, and an artifact falls into that area, it cannot be sourced with certainty using those elements; thus, elements must be identified which exhibit separation between the sources being scrutinized. Trace elements, rather than minor or major elements, often provide less ambiguous source assignments as they often vary in concentration between sources, even those in close geographic and/or geologic context (see Chapter 2). No two obsidian sources will have exactly the same composition, as each has formed in a unique manner; thus some difference will exist between even the most similar of obsidians. It is understandable, though, that some researchers prefer to utilize complex statistical methodologies in obsidian sourcing determinations, as statistical calculations can provide more "mathematical assurance" of source assignments, especially when dealing with sources of similar chemistry (Glascock 1994). However, it is still of utmost importance to identify elements which provide separation between the sources being scrutinized.

The statistical methodology utilized in obsidian sourcing studies has tended to grow more complex over time, although the use, and complexity of the statistics used, has varied with the researcher(s). The methodology generally ranges from simple, using comparisons of chemical compositions or ranges of compositions for the artifacts and source samples (for example: Brown et al. 2004; Dahl et al. 1990; Stross et al. 1977; Stross et al. 1983), to increasingly more mathematically complex, from calculating N-dimensional space plots (with N varying from the number of sources (for example: Reeves and Ward 1976) to the number of elements used in the comparison (for example: Zeitlin and Heimbuch 1978)), to utilizing discriminant analysis (for example: Ericson and Kimberlin 1977; Nelson et al. 1978; Sidrys and Kimberlin 1979), or previously-prepared statistical programs (for example: Negash and Shackley 2006:5; Peterson et al. 1994:165-166), to the rather involved series of statistical procedures utilized at the

Missouri University Research Reactor, which includes cluster analysis, principal components analysis, and canonical discriminant analysis (Glascock 1994:119).

To summarize Glascock (1994), statistical methods are employed to differentiate between the ever-increasing number of sources, especially between sources of similar chemistry, by grouping and/or separating data points, delineating between and/or defining source sample population "spaces," and ultimately, to provide more "mathematical assurance" of correct assignment. And although numerous recent studies utilize statistics of some type to determine (or ensure) source assignments, not all do; for example, Brown et al. (2004) used a series of plots, two bivariate (Zr versus Rb, Zr versus Sr), one trivariate, or ternary (Ti versus Mn versus total Fe (FeO + Fe_2O_3)), and a histogram (Fe/Mn ratios), which were "sufficient … to provide separation between otherwise similar geologic obsidians." However, that particular study was conducted on obsidian artifacts from Belize, thus involved Central American obsidian sources of which only 21 are known (see Chapter 3). It may be a different story in the American Southwest (Arizona and New Mexico) and northern Mexico (Sonora and Chihuahua) area with over 40 known obsidian sources (Shackley 2005:97), and sourcing artifacts from that area may need to take into account more complex movement of material (Peterson et al 1994:165). However, it is at the researchers' discretion whether to perform statistical analyses when conducting obsidian geochemical sourcing studies; further study may indicate whether statistical analyses may indeed be necessary, even in apparently less-complex areas.

Sourcing Methodology Used in This Study

The sourcing methodology utilized in this current study is that of plotting (in element versus element plots) the obsidian debitage sample data and source sample data, using likely sources near the area from which the artifacts were excavated, and visually comparing this information. Central American obsidian sources were compared to the 96 obsidian debitage pieces first, as these sources are located closest to the archaeological sites; as 1 artifact remained without provenance, a number of Mexican obsidian sources were also compared, with no further comparisons needed after this. Certain elements tend to be more useful for obsidian sourcing studies than others, and of the 28 elements analyzed here, the 6 major elements (Al, Ca, Fe, K, Mg, and Na), were initially thought not to be particularly useful, as these can be somewhat variable, even within the same obsidian flow and not included in plots at the outset. The source sample data points for the remaining 22 elements were plotted, with poor to extremely poor results for 12 minor and trace elements (Cr, Cu, Ga, Li, Nb, Ni, Pb, Tl, V, W, Y, and Zn), meaning their source sample "envelopes" were poorly-constrained. Two of the sources studied here, El Chayal, Guatemala (EC), and Güinope, Honduras (GUIN), had very similar chemistry, and the most notable differences between these 2 sources existed for just 3 of the 28 elements analyzed here: Fe, Mn, and Th (see Chapter 5 and Appendix D). A similar situation existed between GUIN and the Jalapa, Guatemala (JAL), source (although the differences between GUIN and JAL tended not to be as large as between EC and GUIN), and were for the elements: Ba, Th, and U (see Chapter 5 and Appendix D). Nine trace elements (Ba, Ce, Cs, La, Rb, Sr, Ta, Th, and U), one minor element (Mn), and 2 major elements (Fe and K) revealed plotted source "envelopes" that were fairly well- to well-constrained. The debitage data was then added to the element versus element plots for these 12 elements, with fair to very clear artifact associations with the source sample "envelopes" resulting. As the artifact associations, and non-associations, with certain sources were clear in this study (see Chapter 5 and Appendix D), the use of further statistical analysis was deemed unnecessary.

CHAPTER 5
OBSIDIAN SOURCING RESULTS

The ultimate goal of this study was determination of the source materials for the 96 obsidian artifacts (debitage pieces), and trace element plots were the main tool used to accomplish this. All 20 known obsidian sources in Central America for which chemical data could be obtained, and 11 selected sources in Mexico, were compared to the debitage pieces, with the associations determined to be: 4 pieces to Ixtepeque, Guatemala, 1 to La Esperanza, Honduras, 1 (tentatively) to Guadalupe Victoria, Mexico, and 90 (tentatively) to Güinope, Honduras, and/or Jalapa, Guatemala. Nine trace elements (Ba, Ce, Cs, La, Rb, Sr, Ta, Th, and U) were found to be particularly useful for accomplishing the source determinations here, with Fe and Mn playing important roles in providing separation between 2 sources with similar chemistry.

Comparison of Trace Element Compositional Data

The compositional data for the 96 obsidian debitage pieces used in the comparisons performed in this study were obtained as a part of this study, and are presented in Table C-1, Appendix C. The chemical data utilized here for the obsidian sources were gathered from a number of sources, and are summarized in Table D-1, Appendix D (the list of sources from which this data was gleaned is given in Appendix D also). As discussed in more detail in Appendix D, the chemical data for 5 important Central American obsidian sources were plotted in a number of element versus element plots (especially using trace elements), with the data for the debitage then added to these plots to see if any might associate with these 5 sources. Some initial associations were apparent, such as 1 piece with La Esperanza (ESP), Honduras, 4 pieces with Ixtepeque (IXT), Guatemala, 90 pieces with the grouping of El Chayal (EC), Guatemala, plus Güinope (GUIN), Honduras, 1 piece remained unassociated, and no pieces associated with San Martín Jilotepeque (SMJ), Guatemala. Interestingly, when the chemical data for the remaining Central American sources were added to these plots, these initial associations still held, and the single formerly unassociated piece remained unassociated. When a select number of Mexican obsidian sources were added to the plots to see if the unassociated piece would associate with any of these, one (Guadalupe Victoria) was seen to have somewhat similar chemistry to this piece, although the similarity was not strong, and the association was thus deemed tentative rather than definitive.

Many of the 28 elements analyzed here were either deemed or found to be unsuitable for conducting source determinations in this study, 4 (Al, Ca, Mg, and Na) because they were major elements, and another 12 (Cr, Cu, Ga, Li, Nb, Ni, Pb, Tl, V, W, Y, and Zn) minor and trace elements whose source sample "envelopes" were poorly-constrained in element versus element plots. Unexpectedly, both Fe and Mn played important roles here, as they (along with Th) revealed separations between 2 sources with extremely similar chemistry (EC and GUIN). Nine trace elements (Ba, Ce, Cs, La, Rb, Sr, Ta, Th, and U), a minor element (Mn), and 2 major elements (Fe and K), yielded plots with fairly well- to well-constrained source sample "envelopes," thus were used in the comparisons performed here. Upon adding the data for the 96 obsidian debitage pieces to these plots, fair to very clear artifact associations, and non-associations, with the source sample "envelopes" resulted, as mentioned above.

Results and Interpretations

Compositional data for all 20 "known" Central American obsidian sources were first compared to the chemical data for the 96 obsidian debitage pieces, as these sources are located closest to the archaeological sites from which the artifacts were unearthed, with a select number (11 of the 66 known) of Mexican obsidian sources also compared (see Chapter 3). Nearly all of these sources were found to have compositions falling significantly enough outside those of the debitage pieces and were eliminated as potential source materials for them (see Appendix D). Such decisions were made on a source-by-source, element-by-element basis, with a number of sources being eliminated by as few as 3 elements (for example Santa Ana Volcano, El Salvador, and Luisitio, Nicaragua), and several by up to as many 9 elements (for example El Paraiso, Honduras, and Zacuáltipan, Mexico), although most sources were eliminated by a combination of 3-4 elements, sometimes more (see Appendix D for more information).

Please see the Rubidium versus Cesium plot (Figure 5) for the next group of comments. This plot was selected as it shows a great many important details. 1) Clear

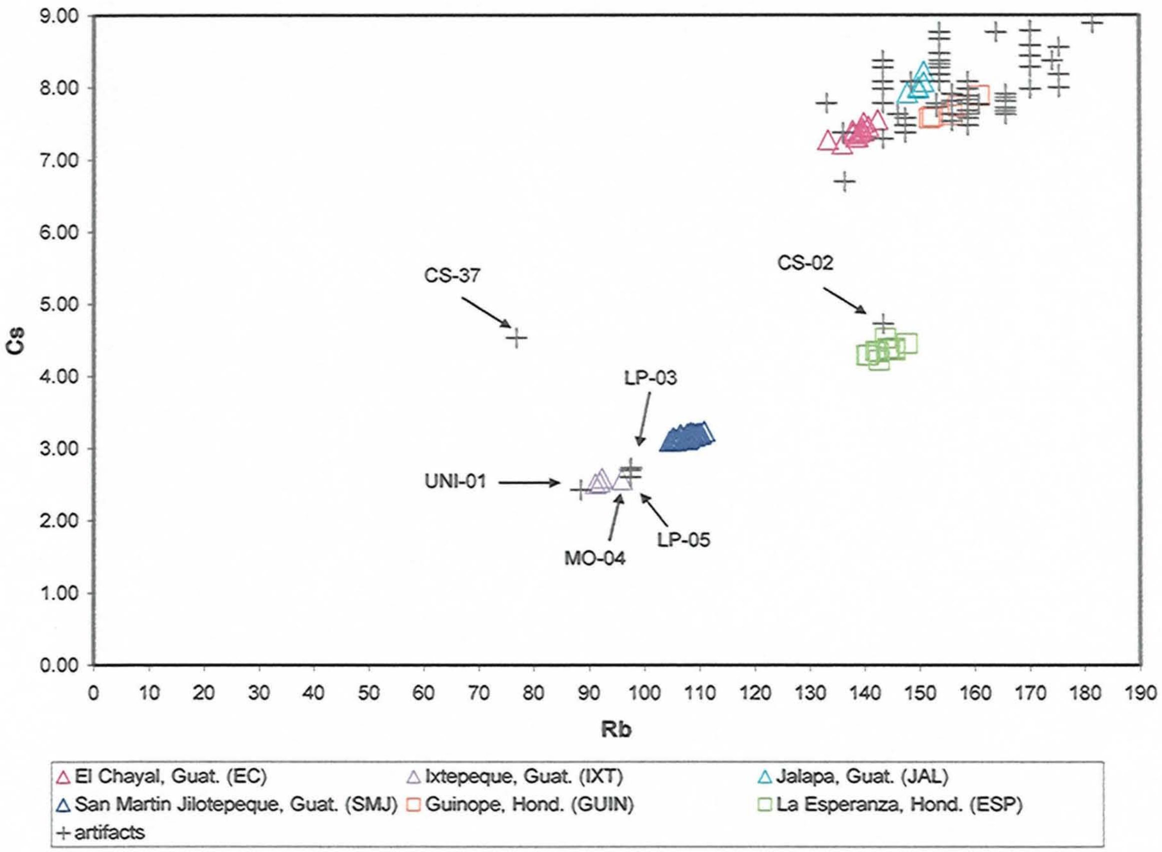


Figure 5. Rubidium versus Cesium plot (in ppm) for all 96 obsidian debitage pieces and 6 likely Central American obsidian sources included in this study.

distinctions or separations are seen between the elemental abundance ranges for both Rb and Cs for the 3 source sample populations of IXT, SMJ, ESP, as well as between these and the "cloud" formed by the somewhat overlapping elemental abundances for both elements for the EC, GUIN, and Jalapa (JAL), Guatemala, source sample populations plus 90 debitage samples. 2) One debitage sample (CS-02) clearly associates with the ESP source sample population (Simmons et al. 2003), and it continues to associate with ESP as clearly, or very nearly so, in all other plots involving Ba, Ce, Cs, La, Rb, Sr, Ta, Th, and U, as well as Fe and Mn. 3) Four debitage samples (LP-03, LP-05, UNI-01, and

MO-04) all clearly associate with the IXT source sample population (Simmons et al. 2003), and these all continue to associate with IXT as clearly, or very nearly so, in all other plots involving those very same 11 elements. 4) One debitage sample (CS-37) consistently does not associate with any known Central American sources. Although preliminary comparison against 11 selected Mexican obsidian sources revealed it to be somewhat similar to Guadalupe Victoria, it has been tentatively (not definitively) assigned to this source, as this association is not strong, and has not been confirmed. In addition, calculated ratios of trace elements to one another for this piece are similar to those for EC, GUIN, and JAL, suggesting it may have originated from an as yet unidentified Central American obsidian source similar in chemistry to these 3 sources. And, 5) the EC, GUIN, and JAL source samples were found to have similar chemistry, thus finding some means of distinguishing between them to determine which might, or might not, be source materials for the 90 debitage pieces comprising the "cloud" was critical, and is addressed below.

As mentioned earlier in this chapter, Fe, Mn, and Th appeared to be the only elements for which there was any significant difference (>~5%) between EC and GUIN. As can be seen in the Thorium versus Cesium plot (Figure 6), Th values for the EC source sample population set it outside the "cloud." The calculated difference in mean Th values between EC and GUIN source sample populations is ~15%, not a great difference, but together with EC decidedly outside the "cloud," and the differences in Mn mean values (~20%) and Fe mean values (~30%), all this is significant enough to eliminate EC. In Figure 6, there appears to be a slight separation between GUIN and JAL source sample populations, and that JAL is also outside the "cloud." However, Ba, Th, and U appear to be the only elements for which there is much difference (again, >~5%) between these 2 sources, and altogether, these differences (~20%, ~6%, and ~7%, for Ba, Th, and U, respectively) may not be significant enough to eliminate JAL; for all other elements analyzed here, the JAL source samples plot extremely close to, and at times directly on top of, those for GUIN. Therefore, this researcher did not believe eliminating JAL to be appropriate, and thus both GUIN and JAL should be considered potential source materials for all 90 of the debitage pieces comprising the "cloud." In searching the literature, this researcher could not find another instance in which the issue of how to

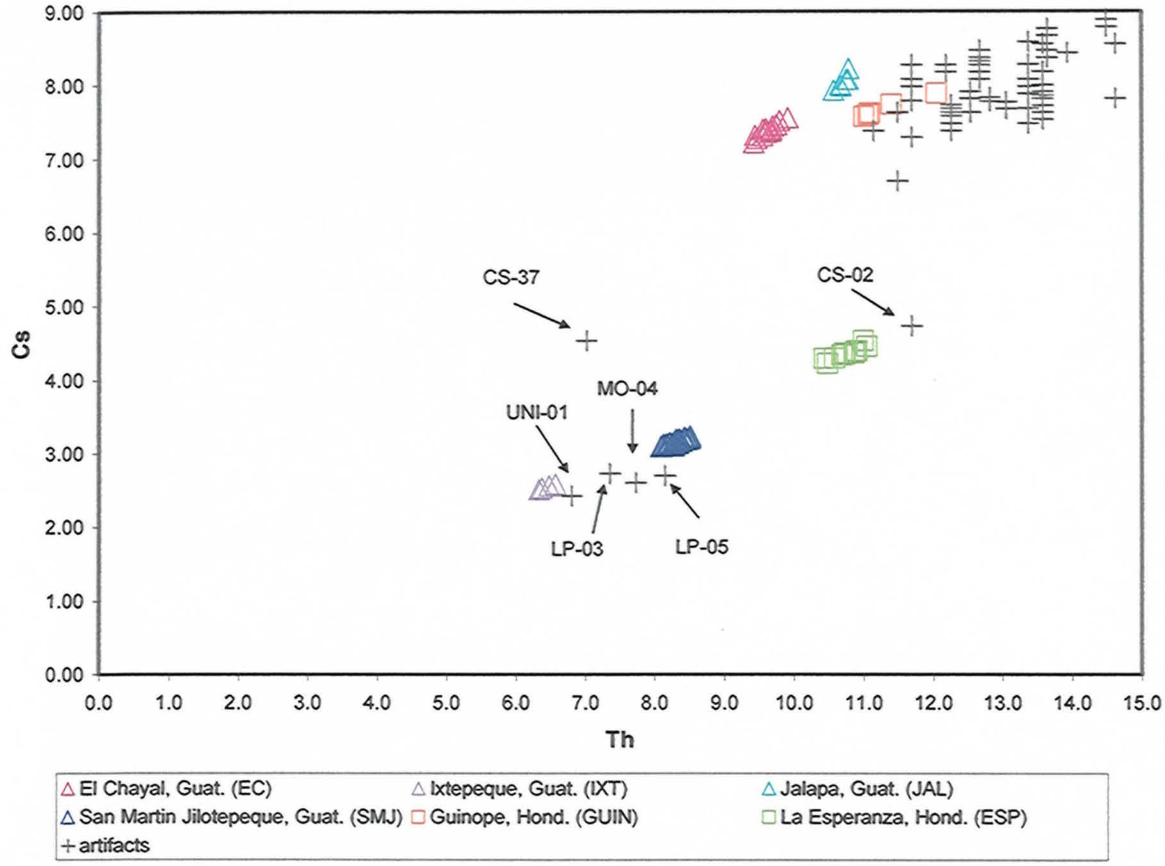


Figure 6. Thorium versus Cesium plot (in ppm) for all 96 obsidian debitage pieces and 6 likely Central American obsidian sources included in this study.

distinguish between GUIN and JAL was even brought up by any other previously-published study (that this researcher came across). It may well be that the particular elements involved in this study simply did not allow for a more definitive separation between these sources, as there are a number of other elements which show greater (or at least a similar degree of) separation, such as: Cl (~25%), Co (~10%), Dy (~8%), Eu (~20%), Gd (~15%), Sb (~9%), Sc (~30%), Sm (~10%), Tb (~18%), Y (~6%), and Zr (~20%) (from data found in: Braswell 1996; Braswell and Glascock 1998; Michael Glascock, written communication 4/22/1997; Glascock et al. 1991; Sheets et al. 1990; Stross et al. 1983; Stross et al. 1992).

The full implications of the results of this study, namely how knowing the sources of these obsidian artifacts affects the understanding of ancient trade routes in this area, are beyond the scope of this study, and are left to archaeologists to determine. However, with 5 obsidian pieces definitively sourced (to 2 separate sources) and 90 likely sourced (to a combination of 2 chemically-similar sources) to Central American obsidian sources, and the final piece potentially sourced to either a Mexican or a yet unidentified Central American obsidian source, this researcher can say that the results obtained here are consistent with those obtained in similar studies conducted on artifacts recovered from Central American archaeological sites.

An important concern for geochemical obsidian sourcing studies is can be seen in Figures 5 and 6. The "cloud" of 90 debitage pieces determined here to tentatively associate with GUIN and/or JAL not only crowd around these source samples, but also range into both higher and lower elemental contents—these pieces occupy a larger compositional "envelope" than that currently delineated by the source samples. Only 6 chemical analyses for GUIN were known to this researcher (see Appendix D), while those for JAL numbered about 13 or so (6 were used in this study; see Appendix D) thus a number of possible situations may be indicated. A likely possibility is that some (or all) of these debitage pieces were fashioned from a yet unknown source of similar chemistry to both GUIN and JAL; this is entirely possible, as more sources are continually being discovered. Another very likely possibility is that these 90 pieces did indeed originate from GUIN and/or JAL, with one, or both, of these sources actually inhabiting a larger range of compositional values than indicated by the relatively few samples available for study. It is quite likely that a given obsidian was more thoroughly "sampled" during quarrying activities than is represented by current samples for analytical (sourcing) purposes, as ancient peoples likely would, given time and opportunity, have exploited as much of a resource at their disposal as they could. Thus, artifact sample populations may, in potentially numerous cases, yield larger compositional "envelopes" than source sample populations. This may especially be so for obsidian sources that were exhausted during quarrying, leaving behind little artifact-quality obsidian for analysis, and perhaps also those sources with unusually large compositional variations, as not all possible compositions may be represented in sample populations of limited number or extent.

CHAPTER 6

ADDITIONAL WORK: COPPER "DROPLETS"

There was additional work performed during this study, as an unexpected, and possibly unprecedented, discovery was made of tiny, previously-molten droplets of copper attached to the outer surface(s) of 5 of the 96 obsidian debitage pieces studied here. They are attached to both worked (knapped) and unworked surfaces, implying that the working of both obsidian and molten copper had occurred in the same place and at the same time. The external morphology ranged from droplets, oriented like splatters, to more irregular "smears," while the internal morphology is typical of material that had cooled very quickly from a molten state, with dendritic structures, segregated material, and trapped gas bubbles. The overall chemistry of the droplets is >~99% Cu (<1% Fe), with the dendrites and segregated material slightly enriched in Fe (~2%). The ages of the strata from which these artifacts were excavated range approximately 300-1200 AD. This area of Central America has been under-studied, thus few copper artifacts, and little metal-working evidence, have been found. This discovery suggests that there may be more metal-working evidence to be unearthed.

Discovery of the Copper "Droplets"

During cleaning of the 100 artifacts studied here in preparation for chemical analysis (see Appendix A), a number of tiny (<<1 to ~1 mm) rounded to elongate, and some irregular, "droplets" of a copper to coppery-red color were observed attached to the outer surface(s) of 5 of the 96 obsidian debitage pieces. As mentioned in Chapter 3, these 5 pieces were excavated from the Ciudad Sandino (CS) archaeological site, which is comprised of 2 small excavations ~1 km apart (Frederick Lange, written communication 11/2/2000), within metropolitan Managua, Nicaragua. One of these pieces (CS-01) was from the N-MA-37 site, and the other 4 (CS-12, CS-23, CS-26, and CS-27) from the N-MA-12 site (Frederick Lange, written communication 11/2/2000); they were recovered from depths below the surface ranging 0-15 cm (N-MA-37) to 25-55 cm (N-MA-12) (Frederick Lange, written communication 11/2/2000), thus possibly as old as 300 AD to possibly as recent as 1200 AD (Frederick Lange, written communication 11/6/2000).

Morphology of the Copper "Droplets"

The droplets were found attached to both worked (knapped) and unworked (original cooling "crust") outer surfaces of the obsidian artifacts. These droplets likely formed by splattering of molten metallic material onto the pieces of obsidian, which is suggested by 2 factors: 1) the majority of droplets are rounded drops with shortish "tails" (see Figure 7), with a few comprised only of tails, and, 2) all droplets + tails (or just tails) on a given artifact are oriented in nearly the same direction, possibly radially (see Figure 8). The droplets occurring on unworked surfaces are more irregular than those on worked surfaces, possibly resulting from a combination of splattering and smearing. There were no significant scratches observed on the outer surfaces of the droplets, and upon removing the 2 droplets from one piece (as detailed below), nothing was observed to be trapped or caught between the metallic droplets and the surface of the obsidian.

The internal morphology of the droplets was determined by observing the thin sections of 2 droplets using a binocular microscope (using both plane polarized and reflected light), up to 800x magnification, housed in the Geology and Geological Engineering Department, CSM. These 2 thin sections were produced by removing 2 rounded drops from one piece (CS-01) using tweezers, mounting these separately in epoxy on glass slides, and polishing each down to have as flat a surface as possible using a series of ever-finer diamond pastes. Unfortunately, the material comprising the droplets was so soft and easily scratched (being essentially pure copper), that deep scratches developed quite easily during polishing; some could not be removed without also polishing away a great deal of the droplet material itself, and thus numerous scratches are still quite visible in the photomicrographs. The larger droplet was ~1 mm in outer diameter, and hollow, as if it had formed around one gas bubble. The interior space was rounded, though slightly elliptical, and ~0.42 mm in inner diameter. The walls of this droplet varied in thickness from ~0.14 mm at the thickest point to ~0.035 mm at the thinnest. The smaller droplet was ~0.425 mm in outer diameter, and also hollow. However, this thin section looked somewhat like a melted "T" (see Figure 9), just as if the metal had formed around 2 smaller gas bubbles, thus the arms of the "T" were the "arms" around the 2 hollows (each ~0.05 mm in inner diameter), with some material between. The 2 "arms" ranged in thickness from ~0.03 mm to ~0.1 mm.

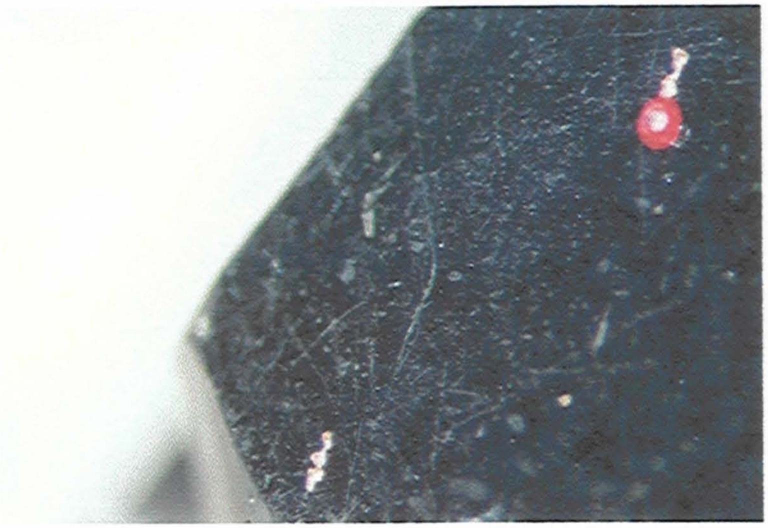


Figure 7. Close-up of obsidian debitage piece CS-27, showing 2 copper "droplets" on its surface. (True-color photograph; ~2x magnification.)

Figure 8. Entire obsidian debitage piece CS-27, with arrows next to each of the 6 copper "droplets" on its surface to emphasize their orientation and direction. Note that all droplets are oriented in nearly the same direction, possibly radial. (True-color photograph; approximately actual size, ~1x).

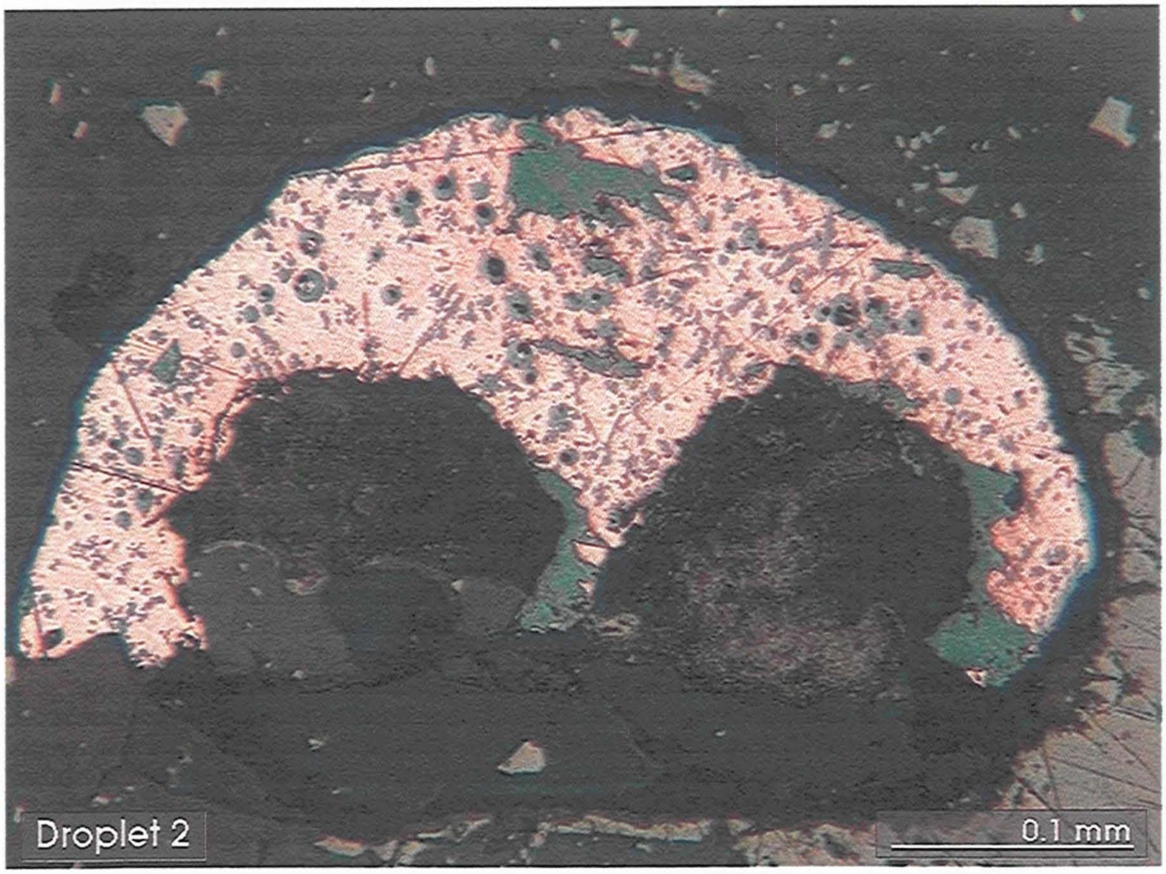


Figure 9. Small copper "droplet" removed from surface of obsidian debitage piece CS-01. Extreme close-up photomicrograph (true-color; magnification ~200x), showing the unusual internal shape of the droplet, having formed around 2 gas bubbles. Note that some scratches developed during polishing are visible.

Upon observing the thin sections of the droplets under reflected light, it was immediately apparent that they consisted of 3 visually- and morphologically-distinct phases (see Figure 10, a true-color extreme close-up photomicrograph of the larger droplet), with the first phase being the copper-colored "matrix," or main phase, in which the other 2 phases reside. The second phase is that of gray, tiny, delicate, dendritic growths, occurring at various angles within the main phase, as well as from the outer (and inner) walls inward into the main phase. The length and width of these dendritic structures varied, from the largest observed (in the larger droplet), ~0.045 mm x ~0.025

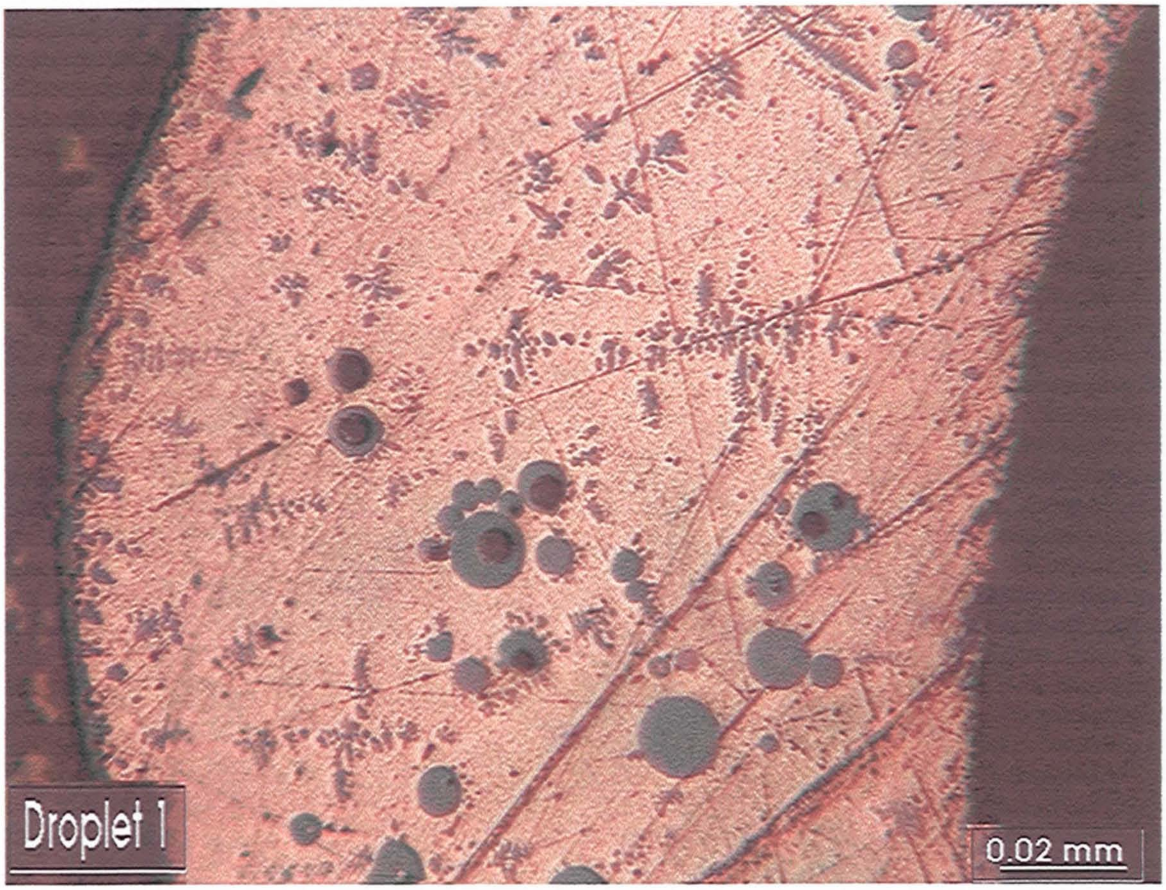


Figure 10. Large copper "droplet" removed from surface of obsidian debitage piece CS-01. Extreme close-up photomicrograph (true-color; magnification ~500x), showing the 3 visually- and morphologically-distinct phases within the droplet (the matrix or main phase, and the dendritic structures and rounded "inclusions" within it). Note that some scratches developed during polishing are visible.

mm, to the smallest being too small to accurately measure. The third phase is that of gray, rounded "inclusions," tending to occur toward the middle of the main phase. Upon closer observation, it could be seen that many of these rounded inclusions have gas bubbles at their centers, thus this material may have coalesced (by segregating from the main phase) around these gas bubbles (Vander Voort 1999). These "inclusions" varied in size, from the largest observed (in either thin section), ~0.013 mm in diameter, to the smallest observed (in either thin section), ~0.0035 mm in diameter.

Composition of the Copper "Droplets"

The composition of metals and ores (especially those that have not been greatly processed or overly alloyed) can yield information regarding their place of origin (see for example: Fraikor et al. 1971; Henderson 2000:248-261; Maddin 1988; Rapp et al. 2000). Elements present in small or trace amounts, such as silver in North American metallic (native) copper deposits (Fraikor et al. 1971; Rapp et al. 2000), or isotopes, such as lead isotopes in copper ores and bronze artifacts in Great Britain (Henderson 2000:253-261), can be indicative of certain areas of formation and/or help distinguish between several possible areas of origin. Thus, in hope of determining the origin of the copper, the chemical compositions of the copper droplets were investigated.

A JEOL 840A Scanning Electron Microscope (SEM), capable of semi-quantitative chemical analysis via Energy Dispersive X-Ray Spectrometry (EDX), housed in the Geology and Geological Engineering Department, CSM, Golden, Colorado, USA, was used for several initial analyses on two droplets (and a tail of 1 of these droplets) still attached to 2 artifacts (CS-23 and CS-27), to obtain preliminary chemical information. SEM data is semi-quantitative, yielding elemental information, but in a relative manner (the height of the peaks in a spectrum (in counts) shows graphically the amounts of each element detected relative to one another in the sample). This data revealed the droplets (and tail) to be essentially 100% Cu, with Fe the only other element detected, and that an extremely minor constituent (see Figure 11). Peaks for Ni are detected (and seen in Figure 11) as this is the main component comprising the sample holder, however the carbon coating on the samples, as needed for accurate analysis, is not detected (John Skok, verbal communication January 2000).

Analyses via a Cameca MBX Electron Microprobe (EMP), housed in the Geology and Geological Engineering Department, CSM, were performed on the 2 thin sections prepared using the 2 droplets removed from the artifact (CS-01) mentioned above; this instrument provides quantitative compositional information. These analyses determined the overall droplet composition to be >~99% Cu, with <1% Fe, and no other elements were detected. The main phase was determined to be ~100% Cu, with <<1% Fe, with no other elements detected. The larger dendritic structures and rounded "inclusion" structures (the smaller dendrites and "inclusions" were too small to yield accurate

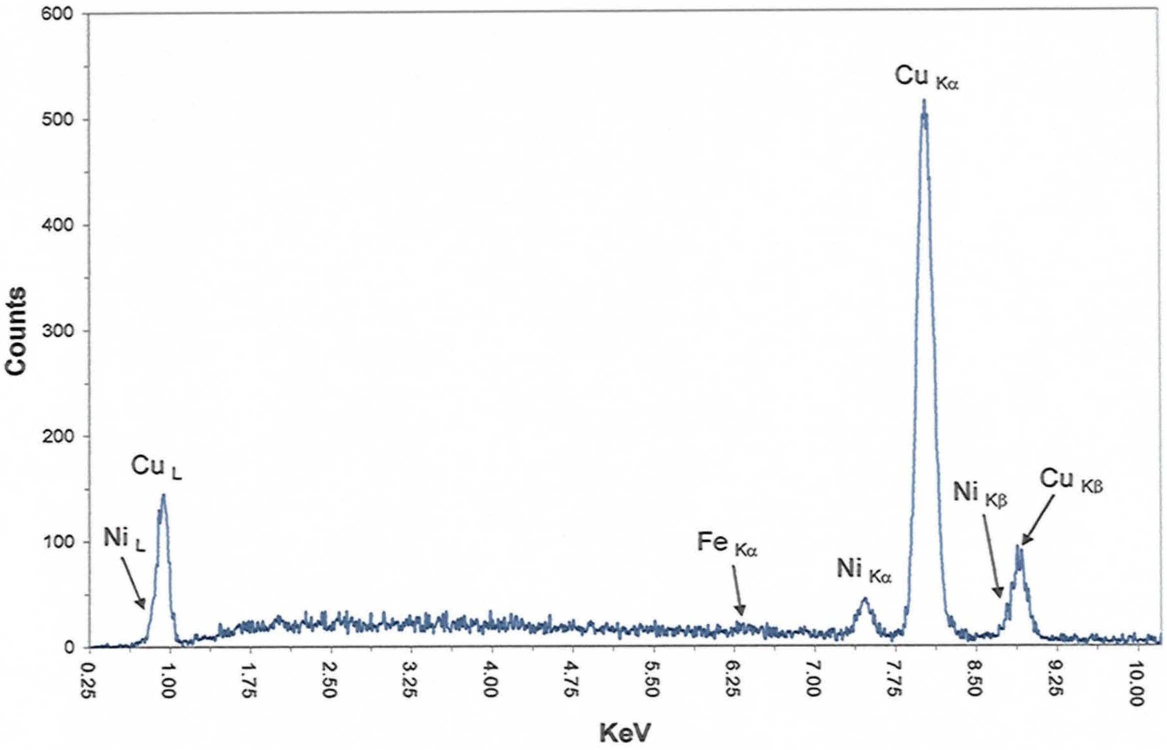


Figure 11. Scanning Electron Microscopy Energy Dispersive X-Ray Spectra for a copper "droplet" attached to obsidian debitage piece CS-23, revealing semi-quantitative (relative) chemical analysis of mostly copper with extremely minor amount of iron. Peak heights convey the relative amounts of each element detected. Note that nickel is detected as it is the main component of the sample holder.

analyses) were revealed to be slightly enriched in Fe (~2%) as compared to the main phase, but still of very high Cu content (~98%), with no other elements detected. Dendrites are indicative structures in quickly-cooled materials, and are often of somewhat different composition from the main phase (Henderson 2000:209; Vander Voort 1999). They are essentially incomplete crystals, having starting forming while the bulk of the material is still molten, and the cooling of the molten material occurs so quickly that the chemical components needed to continue their growth cannot reach them and "fill them in" (Henderson 2000:209; Vander Voort 1999). The "inclusions" of segregated material that also often form in cooling melts (including molten metals) are also typically of somewhat different composition from that of the main phase, as chemical components with somewhat different properties tend to aggregate together (Vander Voort 1999).

Implications of the Copper "Droplets"

That these droplets of copper-rich metal were molten immediately prior to their emplacement upon the obsidian artifacts is clear, based upon their external and internal morphologies. There are a number of implications that may be ascribed to the existence of these droplets, including: 1) the working of both obsidian and molten copper had occurred at the same place and at the same time, as all 5 of the obsidian debitage pieces with attached copper droplets were excavated from a single archaeological site (Frederick Lange, written communication 11/2/2000), the droplets were attached to both worked (knapped) and unworked surfaces, and the droplets were emplaced directly upon the obsidian (nothing is entrained or caught between them and the obsidian); 2) the ancient people were working with very pure copper, as the droplets were determined to be pure copper (~100% overall), and thus they had likely been recasting copper-rich pieces or melting native metallic copper (less likely due to lack of detection of other elements, was purifying of smelt-concentrated copper or smelting of copper-bearing ores) (Henderson 2000:208-296); and, 3) the approximate age of the strata containing the Cu-droplet-bearing obsidian artifacts is 300-1200 AD (Frederick Lange, written communication 11/6/2000), a timeframe for which little metal-working evidence has been unearthed in this area of Central America (see for example: Lange 1996a; West 1994:8-13, Note 4).

Archaeoscientists still disagree regarding the timing and manner of the spread of metal-working knowledge and accompanying technology to, and across, Central America. Some believe this spread may have occurred in a fairly straightforward manner northward from Andean South America around 1800 BC (possibly as early as 1500 BC (West 1994:5-6) or 1410 BC (Snarskis 2003:175), or as late as 200 BC (Lange 1992c:430)), across Central America, to Mesoamerica (Mexico) by ~700-900 AD (see for example: Bray 1984:325-327; Graham 1996; Lange 1992c:430; Saunders 2003:27; West 1994:5-12). Still others believe the spread of metal-working knowledge may have been more complex, such as that of copper-working filtering southward from Mexico and that of gold-working northward from South America (for example, Lange 1992c:431), or that copper- (and perhaps other metal-) working knowledge "skipped" most of Central America for quite some time, with it being carried to Mexico first from South America via trade with sea-going vessels, and later filtering to various spots in Central America (see for example: Hosler 1994; West 1994:10-12).

Due to the relative lack of metal-working evidence unearthed in Central American areas thus far, some archaeoscientists remain skeptical that metal-working took place in some areas of Central America at all (for example, West 1994:11, Note 4). Muddling the issue are: 1) the presence of metal items, nuggets, ingots, and ores in archaeological sites and/or contexts that appear to have reached various Central American and southern Mesoamerican areas via trade, likely from South America (see for example: Cooke et al. 2003; Graham 1996; Snarskis 2003; West 1994); and, 2) the existence of likely looted items in museums and private collections whose age and contextual information are forever lost (see for example: Cooke et al. 2003; Graham 1996; Snarskis 2003; West 1994). However, there numerous deposits of copper throughout Central America, including types that might have been exploited by ancient peoples, namely placers and veins (of numerous types, such as those containing native copper, or sulphides or oxides of copper) (see for example: Cooke et al. 2003:98-101, 106-108, 132-133, 142-144; Fernández and Quintanilla 2003:222-223; Ibarra 2003:386-389; Weyl 1980:293-320). It is unfortunate that the composition of the copper droplets discovered on the artifacts studied here could not precisely pinpoint their origin. However, there remains much area still to be explored, examined, and excavated in Central America, especially in Nicaragua and Honduras (Lange 1992c, 1996a; Maddin 1988; Willey 1984). For example, the 5 archaeological sites studied here were quite small (see Chapter 3), and may even be categorized as "test pits" (Frederick Lange, verbal communication November 1999). More evidence of metal-working may yet remain, still buried and undiscovered, not only in Nicaragua, but in much of Central America.

CHAPTER 7
CONCLUSIONS

The goal of this study was the determination of provenance for 96 obsidian debitage pieces excavated from 5 small archaeological sites located in and near metropolitan Managua, Nicaragua. This was accomplished by first determining the chemical compositions of the pieces via ICP-MS, then comparing these data to the compositions of sources of obsidian in Central America using element versus element plots. Previously-molten droplets of nearly pure copper were unexpectedly found attached to 5 of the 96 obsidian pieces, all from just one of the 5 sites, and these were studied also. Below are presented conclusions for this study as well as a number of recommendations for further study.

Conclusions

The conclusions drawn from this study are:

1) Trace elements were effective for sourcing the obsidian artifacts studied here, with the most effective being: Ba, Ce, Cs, La, Rb, Sr, Ta, Th, and U. The element versus element plots led to definitive source determinations for 5 debitage pieces (4 to the Ixtepeque, Guatemala, source (IXT), and 1 to the La Esperanza, Honduras, source (ESP)), but more tentative determinations for the remaining 91 pieces. The El Chayal, Guatemala (EC), Jalapa, Guatemala (JAL), and Güinope, Honduras (GUIN), sources had very similar chemistry, and only a few of the elements analyzed here were helpful in distinguishing between these sources: Fe, Mn, and Th helped distinguish EC from GUIN, and also eliminated EC as a possible source material; Ba, Th, and U appeared to be the only elements with more than a small difference between GUIN and JAL, and this was not enough to justify eliminating JAL as a possible source material. Ninety of the 91 artifacts tended to form a somewhat disperse "cloud" around the mixture of the both quite small GUIN and JAL source sample populations, and may represent the potentially much larger "sampling" variation that may have occurred during prehistoric tool production for one or

both of these sources; these 90 are tentatively assigned to "GUIN and/or JAL," as these 2 sources are virtually indistinguishable. One debitage piece (CS-37) persistently did not associate with any of the Central American sources, although preliminary comparison against a number of Mexican obsidian sources revealed it to be somewhat similar to the Guadalupe Victoria source, and is thus tentatively assigned it. However, trace element ratios suggest this piece may have originated from an as yet unidentified Central American obsidian source.

2) Trace element versus trace element plots were effective for sourcing the obsidian debitage pieces studied here.
3) Performing statistics on the chemical data may not lead to more definitive assignments for the "cloud" of 90 obsidian debitage pieces tentatively assigned to "GUIN and/or JAL." As mentioned in #1 above, these 2 sources are very similar chemically, and the debitage "cloud" ranges over both these sample populations. It is likely the elements analyzed here were insufficient for providing clear separation between these 2 sources, as elements presented in other publications reveal greater separation between them. However, performing statistics regarding the tentative assignment of CS-37 to Guadalupe Victoria may upgrade, or downgrade, this assignment.
4) The existence of droplets of previously-molten copper on 5 obsidian debitage pieces from just 1 of the 5 archaeological sites studied here implies that the working of both obsidian and molten copper had occurred at the same place and time (~300-1200 AD). Their external morphology is rounded drops with "tails," arranged in splatters, while their internal morphology is typical of quickly-cooled molten material, with dendrites, segregated material and trapped gas bubbles. Their overall composition is >~99% Cu with <1% Fe (no other elements), although the dendrites and inclusions are slightly enriched in Fe (~2%). Very likely these droplets were emplaced onto the obsidian debitage pieces via splattering of molten metal, probably during recasting of copper-rich pieces or smelting of native copper metal.

Recommendations for Further Study

At the beginning of this study, this researcher had thought that little more could be contributed to geochemical obsidian provenance studies, other than items labeled #4 and #5 below, as this area of study is not at all new. However, a number of areas were identified as needing attention or improvement, including the need to increase "standardization" among and between studies. Therefore, recommendations and suggestions for possible further study include:

1) Two obsidian sources involved in this study (GUIN and JAL) had such similar compositions that discriminating between them in order to make definitive sourcing determinations for most of the debitage pieces studied here was not possible (see Chapter 5). Indeed, this author found only 3 elements (Ba, Th and U) for which the differences between the sample population means for these sources were significant (>~5%). However, this author did not come across any previous studies in which the similar chemistry of these 2 sources seemed to be a problem, thus it may well be the case that the elements analyzed here were insufficient for providing separation between them.
2) As noted in Chapter 4, the current methodology for conducting geochemical obsidian provenance studies is to compare compositional data for artifacts to potential sources (either via numbers or plots). However, which elements are used, the number of elements used, and how the elements are used (as numbers, plots, or even ratios), are up to the researcher or institution, perhaps even what analytical instrumentation or facilities were available. A number of recommendations for future study are listed below, the results of which may assist in addressing some as yet unanswered questions, or in bringing more consistency to obsidian provenance studies, possibly ultimately some sort of standardization. It is hoped, by numerous researchers, that a list of "best elements" for obtaining the most consistent and reliable results for all geochemical obsidian studies will ultimately be developed; though this may never be the case (see #4), some partial list of this type may be developed.
    a) Obtaining complete compositional data (especially for trace elements) of all currently known obsidian sources.

b) Concentrating on trace elements, and utilizing minor and major elements secondarily, in conducting geochemical obsidian provenance studies.

c) Comparing the effectiveness of sourcing via compositional ranges versus compositional plots to determine which technique truly is more effective, efficient, and reliable, or whether it varies, and if so, how and/or why.

d) Conduct comparisons of various statistical methodologies on the same series of data sets, especially including such data as different numbers of obsidian sources, sources with similar chemistry, sources with wide internal variations in chemistry, etc., to determine which method(s) or combination of methods may truly be "best" for which situations, and what statistics may be best suited for each scenario.

e) Re-evaluate a number of previous studies, to use different elements (especially to now emphasize trace elements), or a different method of evaluation, or a different instrument, or different statistical methods. Double-check results from previous studies to determine if previously-determined associations of certain artifacts with certain sources still hold, especially if more obsidian sources have been found in the area, or if other elements are evaluated, etc.

f) Conduct an extremely thorough sampling of a known obsidian quarry to ascertain not only the full geochemical variation in the remaining artifact-quality obsidian, but also the possible variation that may be seen in the artifacts that had been fashioned from that source. Revisit how the breadth of source sample population envelopes are determined.

g) After conducting the study suggested in #2-F above, compare the full source compositional results to the composition of all obsidian artifacts assigned to that source to date to see how they compare.

3) Determine exactly what elements, ratios, and plots have been useful for identifying obsidian sources, distinguishing between obsidian sources of similar chemistry, and in determining artifact associations by compiling an exhaustive list from the very first known study to present-day. As with #2-E above, double-check results from previous studies to determine if these

previously-determined associations still hold, especially if more obsidian sources have been found nearby, if other elements evaluate similarly, etc. Additionally, evaluate this data to determine if certain elements appear to be more "useful" in certain areas of the world over others (see #4 below).

4) Conduct an in-depth study to determine the relationship between the petrogenesis of an area to the geochemistry of the obsidian(s) formed there, as a test study to determine how useful this information may be for future studies. A good example would be Central American volcanoes and obsidians, due to the large number of studies performed on Central American obsidian artifacts and the relatively few obsidian sources in this area; the results from this study could be very useful for future studies, and perhaps even serve as a model for future obsidian provenance studies worldwide. A number of studies have made great strides toward understanding the unique geochemistry of Central American volcanoes and their products; however, information regarding obsidian produced from Central American volcanoes has been sporadic, except those volcanoes which have produced large amounts of artifact-quality obsidian, thus already known to archaeologists. Central American volcanism is mostly back-arc, produced due to subduction of the Cocos and Nazca Plates under the Caribbean Plate, although the geochemistry of the volcanic products suggests their origin has been due to both decompression melting and melting of the subducting slabs (Carr et al. 2007; van Wyk de Vries et al. 2007). In addition, there appears to be a trend of increasing silica (and alkalies) content in the volcanoes farther from the trench (Carr et al. 2007; van Wyk de Vries et al. 2007). Despite this, volcanoes of some distance from one another and different distances from the trench (for instance: EC, GUIN, and JAL), have similar chemical features; an interesting trend that deserves some attention.
5) Evaluate the usefulness of incompatible trace element ratios for determining obsidian artifact assignments; this likely is a Ph.D.-level study. As mentioned in Chapter 2, a number of trace elements are also incompatible with the crystals forming in a cooling magma, and are thus preferentially not

incorporated into them. Although the concentration of incompatible trace elements in the cooling magma tends to increase over time, the ratio of one incompatible element to another in the remaining liquid magma tends to remain fairly constant. As points plotted on element versus element plots mathematically equate to ratios of the elemental values to one another, each element versus element plot is a visual representation of a series of ratios. Although element versus element plots are currently used in determining obsidian artifact assignments, these assignments are really accomplished using a statistical methodology(ies) of some sort, mathematical and/or visual. A greater understanding of the behavior of incompatible trace elements during the cooling of magma may lead to the development of a potentially very valuable method for evaluating the likelihood of obsidian sources for inclusion in given obsidian artifact provenance studies (see also Chapter 1).

6) More excavations are needed in Central American areas, especially Nicaragua and Honduras, as there are many gaps in information for these areas, including metal-working (see Chapters 3 and 6). Due to the relative lack of metal-working, and especially copper-working, evidence unearthed in Central American areas to date (see Chapter 6), more excavations likely will help to further delineate the metal-working timeline in and through the area. As the previously-molten copper droplets attached to 5 obsidian artifacts from one site included in this study might possibly be the only evidence uncovered to date that the working of molten copper occurred in the Managua, Nicaragua, area for the period of ~300-1200 AD, and this site, among others in the Managua area, was quite small, there may yet be an untold amount of metal-working evidence still buried, awaiting discovery.

REFERENCES CITED

Aggen, Kerry L., E. Craig Simmons, Frederick W. Lange, and Frederick Fraikor
2000 Molten Copper Droplets upon Obsidian Artifacts from an Archaeological Site in Managua, Nicaragua. *Geological Society of America Abstracts with Programs* 32(7):A-424.

Allègre, C. J., and J. F. Minster
1978 Quantitative Models of Trace Element Behavior in Magmatic Processes. *Earth and Planetary Science Letters* 38:1-25.

Anderson, Anne
1985 *Interpreting Pottery.* Pica Press, New York. 210 pages.

Andrefsky, William, Jr.
2005 Lithic Studies. In *Handbook of Archaeological Methods, Vol. II*, edited by Herbert D. G. Maschner and Christopher Chippendale, pp. 715-772. Altamira Press, Lanham, Maryland. 1469 pages total (2 volumes).

Andrews, Anthony P., Frank Asaro, Helen V. Michel, Fred H. Stross, and Pura Cervera Rivero
1989 The Obsidian Trade at Isla Cerritos, Yucatán, Mexico. *Journal of Field Archaeology* 16:355-363.

Anovitz, Lawrence M., J. Michael Elam, Lee R. Riciputi, and David R. Cole
1999 The Failure of Obsidian Hydration Dating: Sources, Implications, and New Directions. *Journal of Archaeological Science* 26(7):735-752.

Aoyama, Kazuo, Toshiharu Tashiro, and Michael D. Glascock
1999 A Pre-Columbian Obsidian Source in San Luis, Honduras: Implications For the Relationship Between Late Classic Maya Political Boundaries and the Boundaries of Obsidian Exchange Networks. *Ancient Mesoamerica* 10(2):237-249.

Arth, Joseph G.
1976 Behavior of Trace Elements During Magmatic Processes—A Summary of Theoretical Models and Their Applications. *Journal of Research of the United States Geological Survey* 4(1):41-47.

Asaro, F., H. V. Michel, R. Sidrys, and F. Stross
1978 High-Precision Chemical Characterization of Major Obsidian Sources in Guatemala. *American Antiquity* 43(3):436-443.

Associated Press
2007 Scientists Retrace Indian Trade Routes. Electronic document, http://ajc.com, accessed 10/19/2007.

Bargnesi, Keely, Maribeth Dirksen, and Krystal Hartman
1996 Excavación en el Sitio N-MA-62 (UNI). In *Abundante Cooperacíon Vecinal: La Segunda Temporada del Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 37-48. Managua, Nicaragua. 185 p.

Barker, Alex W., Craig E. Skinner, M. Steven Shackley, Michael D. Glascock, and J. Daniel Rogers
2002 Mesoamerican Origin for an Obsidian Scraper from the Precolumbian Southeastern United States. *American Antiquity* 67(1):103-108.

Barnes, Virgil E., George Edwards, W. A. McLaughlin, Irving Friedman, and Oiva Joensuu
1970 Macusanite Occurrence, Age, and Composition, Macusani, Peru. *Geological Society of America Bulletin* 81:1539-1546.

Bellot-Gurlet, L., G. Poupeau, O. Dorighel, Th. Calligaro, J.-C. Dran, and J. Salomon
1999 A PIXE/Fission-Track Dating Approach to Sourcing Studies of Obsidian Artefacts [sic] in Colombia and Ecuador. *Journal of Archaeological Science* 26(8):855-860.

Best, Myron G.
2003 *Igneous and Metamorphic Petrology.* 2nd ed. Blackwell Publishing, Malden, Massachusetts. 729 pages.

Blatt, Harvey
1992 *Sedimentary Petrology.* 2nd ed. Freeman, New York. 514 pages.

Bouška, Vladimír
1993 *Natural Glasses.* Ellis Horwood Limited, New York. 354 pages.

Braswell, Geoffrey E.
1996 *A Maya Obsidian Source: The Geoarchaeology, Settlement History, and Ancient Economy of San Martín Jilotepeque, Guatemala.* Ph.D. dissertation, Tulane University, New Orleans. University Microfilms, Ann Arbor. 1182 p.

Braswell, Geoffrey E., and Michael D. Glascock
2002 The Emergence of Market Economies in the Ancient Maya World: Obsidian Exchange in Terminal Classic Yucatán, Mexico. In *Geochemical Evidence for Long-Distance Exchange*, edited by Michael D. Glascock, pp. 33-52. Bergin and Garvey, Westport, Connecticut. 282 pages.

Braswell, Geoffrey E., and Michael D. Glascock
1998 Interpreting Intrasource Variation in the Composition of Obsidian: The Geoarchaeology of San Martín Jilotepeque, Guatemala. *Latin American Antiquity* 9(4):353-369.

Bray, Warwick
1984 Across the Darien Gap: A Colombian View of Isthmian Archaeology. In *The Archaeology of Lower Central America*, edited by Frederick W. Lange and Doris Z. Stone, pp. 305-338. University of New Mexico Press, Albuquerque. 476 pages.

Briggs, Paul H., and Allen L. Meier
1999 *The Determination of Forty Two Elements in Geological Materials by Inductively Coupled Plasma-Mass Spectrometry.* Open-File Report No. 99-166. United States Government Printing Office, Washington, D.C. 15 pages.

Brown, David O., Meredith L. Dreiss, and Richard E. Hughes
2004 Preclassic Obsidian Procurement and Utilization at the Maya Site of Colha, Belize. *Latin American Antiquity* 15(2):222-240.

Brown, Marshall, Margaret Krieg, and Christopher Wilmott
1996 La Segunda Temporada en el Sitio Villa Tiscapa (N-MA-36). In *Abundante Cooperacíon Vecinal: La Segunda Temporada del Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 9-36. Managua, Nicaragua. 185 pages.

Cann, J. R., and A. C. Renfrew
1964 The Characterization of Obsidian and its Application to the Mediterranean Region. *Proceedings of the Prehistoric Society* 30:111-133.

Carballo, David M., Jennifer Carballo, and Hector Neff
2007 Formative and Classic Period Obsidian Procurement in Central Mexico: A Compositional Study Using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. *Latin American Antiquity* 18(1):27-43.

Carmichael, I. S. E.
1979 Glass and the Glassy Rocks. In *The Evolution of the Igneous Rocks: Fiftieth Anniversary Perspectives*, edited by H. S. Yoder, Jr., pp. 233-244. Princeton University Press, Princeton, New Jersey. 588 pages.

Carozzi, Albert V.
1993 *Sedimentary Petrography.* Prentice Hall, Englewood Cliffs, New Jersey. 263 p.

Carr, Michael J., Lina C. Patino, and Mark D. Feigenson
2007 Petrology and Geochemistry of Lavas. In *Central America: Geology, Resources and Hazards*, edited by Jochen Bundschuh and Guillermo E. Alvarado, pp. 565-590. Taylor and Francis Group, London. 1311 pages total (2 volumes).

Cobean, Robert H., James R. Vogt, Michael D. Glascock, and Terrance L. Stocker
1991 High-Precision Trace-Element Characterization of Major Mesoamerican Obsidian Sources and Further Analyses of Artifacts from San Lorenzo Tenochtitlan, Mexico. *Latin American Antiquity* 2(1):69-91.

Cobean, Robert H., Michael D. Coe, Edward A. Perry, Jr., Karl K. Turekian, and Dinkar P. Kharkar
1971 Obsidian Trade at San Lorenzo Tenochtitlan, Mexico. *Science* 174:666-671.

Cooke, Richard, Ilean Isaza, John Griggs, Benoit Desjardins, and Luís Alberto Sánchez
2003 Who Crafted, Exchanged, and Displayed Gold in Pre-Columbian Panama? In *Gold and Power in Ancient Costa Rica, Panama, and Colombia: A Symposium at Dumbarton Oaks 9 and 10 October 1999*, edited by Jeffrey Quilter and John W. Hoopes, pp. 91-158. Dumbarton Oaks Research Library and Collection, Washington, D.C. 429 pages.

Craig, Nathan, Robert J. Speakman, Rachel S. Popelka-Filcoff, Michael D. Glascock, J. David Robertson, M. Steven Shackley, and Mark S. Aldenderfer
2007 Comparison of XRF and PXRF for Analysis of Archaeological Obsidian from Southern Perú. *Journal of Archaeological Science*, 13 pages, in press.

Dahl, Peter S., Barbara M. Harkness, and Garry C. Maurath
1990 Trace-Element Analysis of Mayan Obsidian Blades from Yucatan and Campeche Provinces, Mexico. *Chemical Geology* 88(1-2):163-167.

Drolet, Robert P.

1992 The House and the Territory: The Organizational Structure for Chiefdom Art in the Diquis Subregion of the Greater Chiriqui Area. In *Wealth and Hierarchy in the Intermediate Area: A Symposium at Dumbarton Oaks, 10th and 11th October 1987*, edited by Frederick W. Lange, pp. 207-241. Dumbarton Oaks Research Library and Collection, Washington, D.C. 463 pages.

Ericson, J. E., and J. Kimberlin

1977 Obsidian Sources, Chemical Characterization and Hydration Rates in West Mexico. *Archaeometry* 19(2):157-166.

Ewart, A.

1971 Chemical Changes Accompanying Spherulitic Crystallization in Rhyolitic Lavas, Central Volcanic Region, New Zealand. *Mineralogical Magazine* 38:424-434.

Fernández, Patricia, and Ifigenia Quintanilla

2003 Metallurgy, Balls, and Stone Statuary in the Diquís Delta, Costa Rica: Local Production of Power Symbols. In *Gold and Power in Ancient Costa Rica, Panama, and Colombia: A Symposium at Dumbarton Oaks 9 and 10 October 1999*, edited by Jeffrey Quilter and John W. Hoopes, pp. 205-243. Dumbarton Oaks Research Library and Collection, Washington, D.C. 429 pages.

Finlayson, Kerri

1996 Prospección y Excavación Preliminar en la Zona de la Laguna de Moyuá. In *Abundante Cooperacíon Vecinal: La Segunda Temporada del Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 133-149. Managua, Nicaragua. 185 pages.

Flanagan, F. J.

1986 *Reference Samples in Geology and Geochemistry.* United States Geological Survey Bulletin 1582. United States Government Printing Office, Washington, D.C. 70 pages.

Fowler, William R., Jr.

1992 The Historiography of Wealth and Hierarchy in the Intermediate Area. In *Wealth and Hierarchy in the Intermediate Area: A Symposium at Dumbarton Oaks, 10th and 11th October 1987*, edited by Frederick W. Lange, pp. 357-377. Dumbarton Oaks Research Library and Collection, Washington, D.C. 463 pages.

Fowler, William R., Jr., Arthur A. Demarest, Helen V. Michel, Frank Asaro, and Fred Stross
1989 Sources of Obsidian from El Mirador, Guatemala: New Evidence on Preclassic Maya Interaction. *American Anthropologist* 91(1):158-168.

Fraikor, Arlene L., James J. Hester, and Frederick J. Fraikor
1971 Metallurgical Analysis of a Hopewell Copper Earspool. *American Antiquity* 36(3):358-361.

Friedman, Irving, and William Long
1984 Volcanic Glasses, Their Origins and Alteration Processes. *Journal of Non-Crystalline Solids* 67:127-133.

Friedman, Irving, and Robert L. Smith
1960 A New Dating Method Using Obsidian: Part 1, The Development of the Method. *American Antiquity* 25:476-522.

Geological Society of America (GSA)
1995 *The Geological Society of America Rock Color Chart, with Genuine Munsell Color Chips*. 8th ed. Geological Society of America, Boulder, Colorado. 14 pages, including 6 plates of color chips.

Glascock, Michael D. (editor)
2002 *Geochemical Evidence for Long-Distance Exchange*. Bergin and Garvey, Westport, Connecticut. 282 pages.

Glascock, Michael D.
1999 An Inter-Laboratory Comparison of Element Compositions for Two Obsidian Sources. *International Association of Obsidian Studies Bulletin* 23:13-25.

Glascock, Michael D.
1997 Written Communication, 4/22/1997. Senior Scientist and Group Leader, Archaeometry Laboratory, Missouri University Research Reactor (MURR), University of Missouri, Columbia, Missouri.

Glascock, Michael D.
1994 New World Obsidian: Recent Investigations. In *Archaeometry of Pre-Columbian Sites and Artifacts: Proceedings of a Symposium Organized by the UCLA Institute of Archaeology and the Getty Conservation Institute, Los Angeles, California, March , 23-27, 1992*, edited by David A. Scott and Pieter Meyers, pp. 113-134. Getty Conservation Institute, Marina Del Rey, California. 421 pages.

Glascock, Michael D., Geoffrey E. Braswell, and Robert H. Cobean
1998 A Systematic Approach to Obsidian Source Characterization. In *Archaeological Obsidian Studies: Method and Theory*, edited by M. Steven Shackley, pp.15-65. Plenum Press, New York. 243 pages.

Glascock, M. D., J. M. Elam, and K. Aoyama
1991 Provenience Analysis of Obsidian Artifacts From the La Entrada Region, Honduras. In *Archaeometry '90: Proceedings of the 27th International Symposium on Archaeometry held in Heidelberg April 2-6, 1990*, edited by Ernst Pernicka and Günther A. Wagner, pp. 395-404. Birkhäuser Verlag, Basel, Boston. 843 pages.

Glascock, M. D., J. M. Elam, and R. H. Cobean
1988 Differentiation of Obsidian Sources in Mesoamerica. In *Archaeometry '88: Proceedings of the 26th International Archaeometry Symposium*, edited by R. M. Farquhar, R. G. V. Hancock, and L. A. Pavlish, pp. 245-251. University of Toronto. 273 pages.

Glascock, M. D., H. Neff, K. S. Stryker, and T. N. Johnson
1994 Sourcing Archaeological Obsidian by an Abbreviated NAA Procedure. *Journal of Radioanalytical and Nuclear Chemistry Articles* 180(1):29-35.

González Rivas, Rafael, Jorge Zambrana Fernández, and Bayardo Gámez Montenegro
1996 Excavaciones en Ciudad Sandino (N-MA-12). In *Abundante Cooperacíon Vecinal: La Segunda Temporada del Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 79-84. Managua, Nicaragua. 185 pages.

Gordus, A. A., W. C. Fink, M. E. Hill, J. C. Purdy, and T. R. Wilcox
1967 Identification of the Geologic Origins of Archaeological Artifacts: An Automated Method of Na and Mn Neutron Activation Analysis. *Archaeometry* 10:87-96.

Govindaraju, K.
1994 1994 Compilation of Working Values and Sample Descriptions for 383 Geostandards. *Geostandards Newsletter* 18:1-158. Special Issue.

Govindaraju, K.
1984 1984 Compilation of Working Values and Sample Descriptions for 170 International Reference Samples of Mainly Silicate Rocks and Minerals. *Geostandards Newsletter* 8:3-16. Special Issue (includes 4 appendices).

Graham, Mark Miller
1996 Merchants and Metalwork in Middle America. In *Paths to Central American Prehistory*, edited by Frederick W. Lange, pp. 237-252. University Press of Colorado, Niwot, Colorado. 379 pages.

Hall, Anthony
1996 *Igneous Petrology*. 2nd ed. Longman House, Harlow, England. 551 pages.

Hanson, Gilbert N.
1980 Rare Earth Elements in Petrogenetic Studies of Igneous Systems. *Annual Review, Earth and Planetary Sciences* 8:371-406.

Hanson, Gilbert N.
1978 The Application of Trace Elements to the Petrogenesis of Igneous Rocks of Granitic Composition. *Earth and Planetary Science Letters* 38:26-43.

Harris, Joan Marie
1986 Silicic Volcanics of Volcán Tequila, Jalisco, México. Unpublished M.S. Thesis, Department of Geology and Geophysics. University of California, Berkeley, California. 98 pages.

Haskin, Larry A.
1984 Petrogenetic Modelling – Use of Rare Earth Elements. In *Rare Earth Element Geochemistry*, edited by Paul Henderson, pp. 115-152. Developments in Geochemistry, Vol. 2. Elsevier Science, Amsterdam, The Netherlands. 510 pages.

Healy, Paul F., Frank Asaro, Fred Stross, and Helen Michel
1996 Precolumbian Obsidian Trade in the Northern Intermediate Area: Elemental Analysis of Artifacts From Honduras and Nicaragua. In *Paths to Central American Prehistory*, edited by Frederick W. Lange, pp. 271-284. University Press of Colorado, Niwot, Colorado. 379 pages.

Healy, Paul F., Heather I. McKillop, and Bernie Walsh
1984 Analysis of Obsidian from Moho Cay, Belize: New Evidence on Classic Maya Trade Routes. *Science* 225:414-417.

Heizer, Robert F., Howel Williams, and John A. Graham
1965 Notes on Mesoamerican Obsidians and Their Significance in Archaeological Studies. In *Sources of Stones Used in Prehistoric Mesoamerican Sites*, pp. 94-103. Contributions of the University of California Archaeological Research Facility No. 1. University of California, Berkeley. 103 pages.

Henderson, Julian
2000 *The Science and Archaeology of Materials: An Investigation of Inorganic Materials*. Routledge, London. 334 pages.

Hester, Thomas R., Robert N. Jack, and Alice Benfer
1973 Trace Element Analyses of Obsidian from Michoacan, Mexico: Preliminary Results. In *Studies in Ancient Mesoamerica*, pp. 167-176. Contributions of the University of California Archaeological Research Facility No. 18. University of California, Berkeley. 188 pages.

Hosler, Dorothy
1994 *The Sounds and Colors of Power: The Sacred Metallurgical Technology of Ancient West Mexico*. Massachusetts Institute of Technology, Cambridge. 310 p.

Hughes, Richard E., and Robert L. Smith
1993 Archaeology, Geology, and Geochemistry in Obsidian Provenance Studies. In *Effects of Scale on Archaeological and Geoscientific Perspectives*, edited by Julie K. Stein and Angela R. Linse, pp. 79-91. Geological Society of America Special Paper 283. Geological Society of America, Boulder, Colorado. 91 pages.

Hurtado de Mendoza, Luis, and William A. Jester
1978 Obsidian Sources in Guatemala: A Regional Approach. *American Antiquity* 43(3):424-435.

Ibarra, Eugenia
2003 Gold in the Everyday Lives of Indigenous Peoples of Sixteenth-Century Southern Central America. In *Gold and Power in Ancient Costa Rica, Panama, and Colombia: A Symposium at Dumbarton Oaks 9 and 10 October 1999*, edited by Jeffrey Quilter and John W. Hoopes, pp. 383-419. Dumbarton Oaks Research Library and Collection, Washington, D.C. 429 pages.

International Association for Obsidian Studies (IAOS)
2007 Obsidian Chemical Information. Electronic Documents, http://www.peak.org/obsidian, last accessed 8/3/2007.

Jack, Robert N., and Robert F. Heizer
1968 "Finger-Printing" of Some Mesoamerican Obsidian Artifacts. In *Papers on Mesoamerican Archaeology*, pp. 81-100. Contributions of the University of California Archaeological Research Facility No. 5. University of California, Berkeley. 203 pages.

Jackson, Julia A. (editor)
1997 *Glossary of Geology.* 4th ed. American Geological Institute, Alexandria, Virginia. 769 pages.

Jackson, Thomas L., and Michael W. Love
1991 Blade Running: Middle Preclassic Obsidian Exchange and the Introduction of Prismatic Blades at La Blanca, Guatemala. *Ancient Mesoamerica* 2:47-59.

Jarvis, K. E., A. L. Gray, and R. S. Houk
1992 *Handbook of Inductively-Coupled Plasma Mass Spectrometry.* Chapman and Hall, New York. 398 pages.

Jennings, Justin, and Michael D. Glascock
2002 Description and Method of Exploitation of the Alca Obsidian Source, Peru. *Latin American Antiquity* 13(1):107-118.

Jezek, Peter A., and Donald C. Noble
1978 Natural Hydration and Ion Exchange of Obsidian: An Electron Microprobe Study. *American Mineralogist* 63:266-273.

Johnstone, Robert A. W., and Malcolm E. Rose
1996 *Mass Spectrometry for Chemists and Biochemists.* 2nd ed. Cambridge University Press, New York. 501 pages.

Kardulias, P. Nick, and Richard W. Yerkes
2003 Introduction: Lithic Analysis as Cross-Cultural Study. In *Written In Stone: The Multiple Dimensions of Lithic Analysis*, edited by P. Nick Kardulias and Richard W. Yerkes, pp. 1-5. Lexington Books, Lanham, Maryland. 143 pages.

Keller, Chad, Charles Lawson, and Ryan Sievers
1996 Excavaciones en Ciudad Sandino (N-MA-37). In *Abundante Cooperacíon Vecinal: La Segunda Temporada del Proyecto "Arqueologia de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 85-98. Managua, Nicaragua. 185 pages.

Lange, Frederick W.
2006 Written Communication, 8/10/2006. Former Director, Anthropological Museum, University of Colorado at Boulder, Boulder, Colorado.

Lange, Frederick W.
2000 Written Communications, 11/2/2000 and 11/6/2000. Former Director, Anthropological Museum, University of Colorado at Boulder, Boulder, Colorado.

Lange, Frederick W.
1999 Verbal Communication, November 1999. Former Director, Anthropological Museum, University of Colorado at Boulder, Boulder, Colorado.

Lange, Frederick W. (editor)
1996 *Abundante Cooperacíon Vecinal: La Segunda Temporada del Proyecto "Arqueología de la Zona Metropolitana de Managua."* Managua, Nicaragua. 185 pages.

Lange, Frederick W.
1996a Gaps in Our Databases and Blanks in Our Syntheses: The Potential for Central American Archaeology in the Twenty-First Century. In *Paths to Central American Prehistory*, edited by Frederick W. Lange, pp. 305-326. University Press of Colorado, Niwot, Colorado. 379 pages.

Lange, Frederick W.
1996b Los Antecedentes y Los Resultados de la Segunda Temporada del Proyecto "Arqueología de la Zona Metropolitana Managua." In *Abundante Cooperacíon Vecinal: La Segunda Temporada del Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 1-8. Managua, Nicaragua. 185 pages.

Lange, Frederick W. (editor)
1995 *Descubriendo las Huellas de Nuestros Antepasados: El Proyecto "Arqueología de la Zona Metropolitana de Managua."* Managua, Nicaragua. 159 p.

Lange, Frederick W.
1995 Los Antecedentes y los Resultados de la Primera Temporada del Proyecto "Arqueología de la Zona Metropolitana de Managua." In *Descubriendo las Huellas de Nuestros Antepasados: El Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 1-8. Managua, Nicaragua. 159 p.

Lange, Frederick W. (editor)
1992 *Wealth and Hierarchy in the Intermediate Area: A Symposium at Dumbarton Oaks, 10th and 11th October 1987.* Dumbarton Oaks Research Library and Collection, Washington, D.C. 463 pages.

Lange, Frederick W.
1992a The Intermediate Area: An Introductory Overview of Wealth and Hierarchy Issues. In *Wealth and Hierarchy in the Intermediate Area: A Symposium at Dumbarton Oaks, 10th and 11th October 1987*, edited by Frederick W. Lange, pp. 1-14. Dumbarton Oaks Research Library and Collection, Washington, D.C. 463 p.

Lange, Frederick W.
1992b The Search for Elite Personages and Site Hierarchies in Greater Nicoya. In *Wealth and Hierarchy in the Intermediate Area: A Symposium at Dumbarton Oaks, 10th and 11th October 1987*, edited by Frederick W. Lange, pp. 109-139. Dumbarton Oaks Research Library and Collection, Washington, D.C. 463 pages.

Lange, Frederick W.
1992c Summary: Perspectives on Wealth and Hierarchy in the Intermediate Area. In *Wealth and Hierarchy in the Intermediate Area: A Symposium at Dumbarton Oaks, 10th and 11th October 1987*, edited by Frederick W. Lange, pp. 423-443. Dumbarton Oaks Research Library and Collection, Washington, D.C. 463 pages.

Le Maitre, R. W. (editor)
2002 *Igneous Rocks: A Classification and Glossary of Terms: Recommendations of the International Union of Geological Sciences, Subcommission on the Systematics of Igneous Rocks*. 2nd ed. Cambridge University Press, England. 236 pages.

Loyd, Janine M., Thomas M. Origer, and David A. Frederickson (editors)
2002 *The Effects of Fire and Heat on Obsidian*. United States Department of the Interior, Bureau of Land Management, Cultural Resources Publication, Anthropology—Fire History. Bishop Field Office, California. 225 pages.

MacDonald, Ray, and D. K. Bailey
1973 Chapter N: Chemistry of Igneous Rocks—Part 1: The Chemistry of the Peralkaline Oversaturated Obsidians. In *Data of Geochemistry,* edited by Michael Fleischer, pp. N1-N37. 6th ed. United States Geological Survey Professional Paper 440-N-1. United States Government Printing Office, Washington, D.C. 37 pages.

Maddin, Robert (editor)
1988 *The Beginning of the Use of Metals and Alloys*. Massachusetts Institute of Technology, Cambridge. 393 pages.

Mahood, Gail, and Wes Hildreth
1983 Large Partition Coefficients for Trace Elements in High-Silica Rhyolites. *Geochimica et Cosmochimica Acta* 47:11-30.

Marshall, Royal R.
1961 Devitrification of Natural Glass. *Geological Society of America Bulletin* 72:1493-1520.

McKillop, H., L. J. Jackson, H. Michel, F. Stross, and F. Asaro
1988 Chemical Source Analysis of Maya Obsidian: New Perspectives from Wild Cane Cay, Belize. In *Archaeometry '88: Proceedings of the 26th International Archaeometry Symposium*, edited by R. M. Farquhar, R. G. V. Hancock, and L.A. Pavish, pp. 239-244. University of Toronto. 273 pages.

Meier, Allen
1999 Verbal Communications 1/12/1999 and 4/22/1999. Research Chemist, United States Geological Survey Crustal Imaging and Characterization Team, Geologic Division, USGS, Denver Federal Center, Lakewood, Colorado.

Michels, J. W.
1982 Bulk Element Composition Versus Trace Element Composition in the Reconstruction of an Obsidian Source System. *Journal of Archaeological Science* 9(2):113-123.

Moholy-Nagy, Hattula
2003 Source Attribution and the Utilization of Obsidian in the Maya Area. *Latin American Antiquity* 14(3):301-310.

Moholy-Nagy, Hattula, Frank Asaro, and Fred H. Stross
1984 Tikal Obsidian: Sources and Typology. *American Antiquity* 49(1):104-117.

Moholy-Nagy, Hattula, and Fred W. Nelson
1990 New Data on Sources of Obsidian Artifacts from Tikal, Guatemala. *Ancient Mesoamerica* 1:71-80.

National Institute of Standards & Technology (NIST)
1993 Certificate of Analysis: Standard Reference Material 2709, San Joaquin Soil. NIST, Gaithersburg, Maryland. 13 pages.

National Institute of Standards & Technology (NIST)
1992 Certificate of Analysis: Standard Reference Material 278, Obsidian Rock. NIST, Gaithersburg, Maryland. 3 pages.

Negash, Agazi, and M. S. Shackley
2006 Geochemical Provenance of Obsidian Artefacts [sic] from the MSA Site of Porc Epic, Ethiopia. *Archaeometry* 48(1):1-12.

Nelson, Fred W., Jr., David A. Phillips, Jr., and Alfredo Barrera Rubio
1983 Appendix A: Trace Element Analysis of Obsidian Artifacts from the Northern Maya Lowlands. In *Investigations at Edzná, Campeche, Mexico; Volume 1, Part 1: The Hydraulic System*, edited by R. T. Matheny, D. L. Gurr, D. W. Forsyth, and F. R. Hauck, pp. 205-219. Papers of the New World Archaeological Foundation No. 46. New World Archaeological Foundation, Brigham Young University, Provo, Utah. 239 pages.

Nelson, Fred W., Raymond V. Sidrys, and Richard D. Holmes
1978 Trace Element Analysis by X-Ray Fluorescence of Obsidian Artifacts from Guatemala and Belize. In *Excavations at Seibal, Department of Peten, Guatemala, No. 1: Artifacts*, edited by G. R. Willey, pp. 153-161. Memoirs of the Peabody Museum of Archaeology and Ethnology Vol. 14. Harvard University, Cambridge, Massachusetts. 189 pages.

Neuendorf, Klaus K. E., James P. Mehl, Jr., and Julia A. Jackson (editors)
2005 *Glossary of Geology.* 5th ed. American Geological Institute, Alexandria, Virginia. 779 pages.

Nickel, Brian K.
1987 The Hydration and Alteration of the Perlite, Pitchstone, and Upper Pyroclastic Unit at Ruby Mountain, Nathrop, Colorado. Unpublished M.S. Thesis. Bowling Green State University, Ohio. 84 pages.

Noble, Donald C.
1967 Sodium, Potassium, and Ferrous Iron Contents of Some Secondarily Hydrated Natural Silicic Glasses. *American Mineralogist* 52:280-286.

Northwest Research Obsidian Studies Laboratory (NROS)
2006 X-Ray Fluorescence Information. Electronic documents, http://www.obsidianlab.com, last accessed 11/26/2006.

Obenauf, Ralph H., Richard Bostwick, William Fithian, Mena DeStefano, and William Mack (editors)
2000 *SPEX CertiPrep Handbook of Sample Preparation and Handling.* 7th ed. SPEX CertiPrep, Inc., Metuchen, New Jersey. 215 pages.

Peterson, Jane, Douglas R. Mitchell, and M. Steven Shackley

1994 Obsidian from Pueblo Grande, Arizona: Modeling Social and Economic Patterns in Lithic Procurement. In *Archaeometry of Pre-Columbian Sites and Artifacts: Proceedings of a Symposium Organized by the UCLA Institute of Archaeology and the Getty Conservation Institute, Los Angeles, California, March, 23-27, 1992*, edited by David A. Scott and Pieter Meyers, pp. 161-173. Getty Conservation Institute, Marina Del Rey, California. 421 pages.

Pichardo Pichardo, Lubi, and Jorge Zambrana Fernández

1995 Prospección y Excavación Arqueológica Sitio N-MA-62 UNI, Managua. In *Descubriendo las Huellas de Nuestros Antepasados: El Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 75-82. Managua, Nicaragua. 159 pages.

Piper, James R.

1994 The Hydration and Geochemistry of Silicic Volcanic Glasses. Unpublished M.S. Thesis, Department of Geology and Geological Engineering, Colorado School of Mines, Golden, Colorado. 97 pages.

Pullen, Heidi

1995 Prospección Arqueológica en Villa Tiscapa Sitio N-MA-36. In *Descubriendo las Huellas de Nuestros Antepasados: El Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 41-50. Managua, Nicaragua. 159 pages.

Rapp, George Robert, James Allert, Vanda Vitali, Zhichun Jing, and Eiler Henrickson

2000 *Determining Geologic Sources of Artifact Copper: Source Characterization Using Trace Element Patterns.* University Press of America, Inc., Lanham, Maryland. 156 pages.

Reeves, Roger D., and Graeme K. Ward

1976 Characterization Studies of New Zealand Obsidians: Toward a Regional Prehistory. In *Advances in Obsidian Glass Studies: Archaeological and Geochemical Perspectives*, edited by R. E. Taylor, pp. 259-287. Noyes Press, Park Ridge, New Jersey. 360 pages.

Rice, Prudence M.

1987 *Pottery Analysis: A Sourcebook.* The University of Chicago Press, Chicago. 559 pages.

Rice, Prudence M., Helen V. Michel, Frank Asaro, and Fred Stross

1985 Provenience Analysis of Obsidians From the Central Peten Lakes Region, Guatemala. *American Antiquity* 50(3):591-604.

Rogers, Alexander K.
2006 Induced Hydration of Obsidian: A Simulation Study of Accuracy Requirements. *Journal of Archaeological Science* 33(12):1696-1705.

Ross, Clarence S., and Robert L. Smith
1961 *Ash-Flow Tuffs: Their Origin, Geologic Relations and Identification.* United States Geological Survey Professional Paper 366. United States Government Printing Office, Washington, D.C. 81 pages.

Rowsey, Janine
2001 The Feasibility of Sourcing Petrified Wood Artifacts in the Denver Basin and Adjacent Foothills. Unpublished M.S. Thesis, Department of Metallurgical and Materials Engineering, Materials Science Program, Colorado School of Mines, Golden, Colorado. 275 pages.

Saunders, Nicholas J.
2003 "Catching the Light": Technologies of Power and Enchantment in Pre-Columbian Goldworking. In *Gold and Power in Ancient Costa Rica, Panama, and Colombia: A Symposium at Dumbarton Oaks 9 and 10 October 1999*, edited by Jeffrey Quilter and John W. Hoopes, pp. 15-47. Dumbarton Oaks Research Library and Collection, Washington, D.C. 429 pages.

Shackley, M. Steven
2002 More Than Exchange: Pre-Ceramic Through Ceramic Period Obsidian Studies in the Greater North American Southwest. In *Geochemical Evidence for Long-Distance Exchange*, edited by Michael D. Glascock, pp. 53-87. Bergin and Garvey, Westport, Connecticut. 282 pages.

Shackley, M. Steven
2005 *Obsidian: Geology and Archaeology in the North American Southwest.* The University of Arizona Press, Tucson. 246 pages.

Sharer, Robert J.
1984 Lower Central America as Seen from Mesoamerica. In *The Archaeology of Lower Central America*, edited by Frederick W. Lange and Doris Z. Stone, pp. 63-84. University of New Mexico Press, Albuquerque. 476 pages.

Sheets, Payson D.
1992 The Pervasive Pejorative in Intermediate Area Studies. In *Wealth and Hierarchy in the Intermediate Area: A Symposium at Dumbarton Oaks, 10th and 11th October 1987*, edited by Frederick W. Lange, pp. 15-39. Dumbarton Oaks Research Library and Collection, Washington, D.C. 463 pages.

Sheets, Payson D.
1984 The Prehistory of El Salvador: An Interpretive Summary. In *The Archaeology of Lower Central America*, edited by Frederick W. Lange and Doris Z. Stone, pp. 85-112. University of New Mexico Press, Albuquerque. 476 pages.

Sheets, Payson, Kenneth Hirth, Fred Lange, Fred Stross, Frank Asaro, and Helen Michel
1990 Obsidian Sources and Elemental Analyses of Artifacts in Southern Mesoamerica and the Northern Intermediate Area. *American Antiquity* 55(1):144-158.

Sheridan, Michael F.
1979 Emplacement of Pyroclastic Flows: A Review. In *Ash-Flow Tuffs*, edited by Charles E. Chapin and Wolfgang E. Elston, pp. 125-136. Geological Society of America Special Paper 180. Geological Society of America, Boulder, Colorado. 211 pages.

Sidrys, Raymond, and Jerome Kimberlin
1979 Use of Mayan Obsidian Sources Through Time: Trace-Element Data from El Balsamo, Guatemala. *Journal of Field Archaeology* 6:116-122.

Simmons, E. Craig
1999 Verbal Communication January 1999. Associate Professor, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado.

Simmons, E. Craig, Kerry L. Aggen, Mark E. Eberhart, and Fred F. Fraikor
2003 Preliminary Sourcing for Obsidian Debitage Associated with Evidence for Metallurgical Activity in Managua, Nicaragua. Paper presented at the 55th Annual Meeting of the Rocky Mountain Section of the Geological Society of America, Fort Lewis, Colorado.

Skinner, Craig Eugene
1983 Obsidian Studies in Oregon: An Introduction to Obsidian and An Investigation of Selected Methods of Obsidian Characterization Utilizing Obsidian Collected at Prehistoric Quarry Sites in Oregon. Unpublished M.S. thesis, Department of Interdisciplinary Studies, University of Oregon. 405 pages total (2 volumes).

Skok, John
2000 Verbal Communication January 2000. Geological Technician, Department of Geology and Geological Engineering, Colorado School of Mines, Golden, Colorado.

Smith, Robert L.

1960 *Zones and Zonal Variations in Welded Ash Flows*. United States Geological Survey Professional Paper 354-F. United States Government Printing Office, Washington, D.C. pp. 149-159.

Snarskis, Michael J.

2003 From Jade to Gold in Costa Rica: How, Why, and When. In *Gold and Power in Ancient Costa Rica, Panama, and Colombia: A Symposium at Dumbarton Oaks 9 and 10 October 1999*, edited by Jeffrey Quilter and John W. Hoopes, pp. 159-204. Dumbarton Oaks Research Library and Collection, Washington, D.C. 429 pages.

Stauber, Daniel M.

1996 Excavaciones Arqueológicas e Investigaciones Preliminares en el Sitio Los Placeres (N-MA-1). In *Abundante Cooperacíon Vecinal: La Segunda Temporada del Proyecto "Arqueología de la Zona Metropolitana de Managua,"* edited by Frederick W. Lange, pp. 49-67. Managua, Nicaragua. 185 pages.

Stross, Fred, Frank Asaro, and Helen Michel

1992 Elemental Analysis of Obsidian Samples from Pacific Nicaragua and from Northwest Costa Rica. In *The Archaeology of Pacific Nicaragua*, by Frederick E. Lange, Payson D. Sheets, Anibal Martinez, and Suzanne Abel-Vidor, pp. 119-134. University of New Mexico Press, Albuquerque. 323 pages.

Stross, F. H., F. Asaro, H. V. Michel, and R. Gruhn

1977 Sources of Some Obsidian Flakes from a Paleoindian Site in Guatemala. *American Antiquity* 42(1):114-118.

Stross, Fred H., Thomas R. Hester, Robert F. Heizer, and Robert N. Jack

1976 Chemical and Archaeological Studies of Mesoamerican Obsidians. In *Advances in Obsidian Glass Studies: Archaeological and Geochemical Perspectives*, edited by R. E. Taylor, pp. 240-258. Noyes Press, Park Ridge, New Jersey. 360 pages.

Stross, Fred H., Payson Sheets, Frank Asaro, and Helen V. Michel

1983 Precise Characterization of Guatemalan Obsidian Sources and Source Determination of Artifacts from Quiriguá. *American Antiquity* 48(2):323-346.

Taylor, Howard E.

2001 *Inductively Coupled Plasma-Mass Spectrometry: Practices and Techniques*. Academic Press, San Diego, California. 294 pages.

Tykot, Robert H.
2003 Determining the Source of Lithic Artifacts and Reconstructing Trade in the Ancient World. In *Written In Stone: The Multiple Dimensions of Lithic Analysis*, edited by P. Nick Kardulias and Richard W. Yerkes, pp. 59-85. Lexington Books, Lanham, Maryland. 143 pages.

United States of America Central Intelligence Agency (USA CIA)
2000 *Map of Central America and the Caribbean.* Cartographic map, 1:12,500,000. USA CIA.

United States Geological Survey (USGS)
Undated. Accepted Values for In-House Standards. Report on file, Mineral Resources Survey Program, USGS, Denver Federal Center, Lakewood, Colorado. 1 page.

United States Geological Survey (USGS)
1995 Certificate of Analysis: Basalt, Hawaiian Volcanic Observatory, BHVO-1. USGS, Denver, Colorado. 2 pages.

United States Geological Survey (USGS)
1995 Certificate of Analysis: Rhyolite, Glass Mountain, RGM-1. USGS, Denver, Colorado. 3 pages.

University of Missouri-Columbia
2007 Electronic documents, http://web.missouri.edu/~umcreactorweb/pages/ac_mdg.shtml, http://web.missouri.edu/~umcreactorweb/pages/ac_naa1.shtml, accessed 10/31/2007.

van Wyk de Vries, Benjamin, Pablo Grosse, and Guillermo E. Alvarado
2007 Volcanism and Volcanic Landforms. In *Central America: Geology, Resources and Hazards*, edited by Jochen Bundschuh and Guillermo E. Alvarado, pp. 123-154. Taylor and Francis Group, London. 1311 pages total (2 volumes).

Vander Voort, George F.
1999 *Metallography: Principles and Practice.* ASM International, Materials Park, Ohio. 752 pages.

Vogt, J. R., C. C. Graham, M. D. Glascock, and R. H. Cobean
1982 A Study of Mesoamerican Obsidian Sources Using Activation Analysis. *Journal of Radioanalytical Chemistry* 69(1-2):271-289.

Watson, J. Throck
1997 *Introduction to Mass Spectrometry.* 3rd ed. Lippincott-Raven Publishers, Philadelphia, Pennsylvania. 496 pages.

Weaver, J. R., and F. H. Stross
1965 Analysis by X-Ray Fluorescence of Some American Obsidians. In *Sources of Stones Used in Prehistoric Mesoamerican Sites*, pp. 89-93. Contributions of the University of California Archaeological Research Facility No. 1. University of California, Berkeley. 103 pages.

West, Robert C.
1994 Aboriginal Metallurgy and Metalworking in Spanish America: A Brief Overview. In *In Quest of Mineral Wealth: Aboriginal and Colonial Mining and Metallurgy in Spanish America*, edited by Alan K. Craig and Robert C. West, pp. 5-20. Geoscience and Man, Vol. 33. Department of Geography and Anthropology Geoscience Publications, Louisiana State University, Baton Rouge. 354 pages.

Weyl, Richard
1980 *Geology of Central America.* 2nd ed. Gebrüder Borntraeger, Berlin. 371 pages.

Willey, Gordon R.
1984 A Summary of the Archaeology of Lower Central America. In *The Archaeology of Lower Central America*, edited by Frederick W. Lange and Doris Z. Stone, pp. 341-378. University of New Mexico Press, Albuquerque. 476 pages.

Wilson, Marjorie
1989 *Igneous Petrogenesis: A Global Tectonic Approach.* Chapman and Hall, London, England. 466 pages.

Winter, John D.
2001 *An Introduction to Igneous and Metamorphic Petrology.* Prentice-Hall, Upper Saddle River, New Jersey. 697 pages.

Xie, Xuejing, Mingcai Yan, Lianzhong Li, and Huijun Shen
1985 Geochemical Reference Samples, Drainage Sediments GSD 1-8 from China. *Geostandards Newsletter* 9(1):83-159.

Yerkes, Richard W.
2003 Using Lithic Artifacts to Study Craft Specialization in Ancient Societies: The Hopewell Case. In *Written In Stone: The Multiple Dimensions of Lithic Analysis*, edited by P. Nick Kardulias and Richard W. Yerkes, pp. 17-34. Lexington Books, Lanham, Maryland. 143 pages.

Yerkes, Richard W., and P. Nick Kardulias
1993 Recent Developments in the Analysis of Lithic Artifacts. *Journal of Archaeological Research* 1(2):89-119.

Zeitlin, Robert N., and Ray C. Heimbuch
1978 Trace Element Analysis and the Archaeological Study of Obsidian Procurement in Precolumbian Mesoamerica. In *Lithics and Subsistence: The Analysis of Stone Tool Use in Prehistoric Economies*, edited by Dave D. Davis, pp. 117-159. Vanderbilt University Publications in Anthropology No. 20, Nashville, Tennessee. 198 pages.

Zielinski, Robert A., Peter W. Lipman, and Hugh T. Millard, Jr.
1976 Minor-Element Variations in Hydrated and Crystallized Calc-Alkalic Rhyolites. In Geological Survey Research 1976: A Summary of Recent Significant Scientific and Economic Results Accompanied By a List of Geologic and Hydrologic Investigations in Progress and a Report on the Status of Topographic Mapping, p. 175. United States Geological Survey Professional Paper 1000. United States Government Printing Office, Washington, D.C. 414 pages.

APPENDIX A
ANALYTICAL METHODOLOGY

This appendix describes the analytical methodology followed in this study, including the processes involved in preparing all samples studied here for chemical analysis, as well as the instrumental methodology used to obtain their chemical analyses. Also included in this Appendix are results obtained from performing optical studies of the 100 artifacts and 3 obsidian flows ("Other Reference Materials"). The samples studied here included 100 artifacts (debitage pieces) of unknown composition, and pieces from 3 obsidian flows whose compositions ranged from unknown to known to a small degree of certainty; also analyzed were 8 geological and geochemical standards, whose compositions ranged from well-characterized to known to a lesser degree of certainty.

The 100 artifacts consisted of 96 pieces of obsidian, 2 pieces of other lithic materials, and 2 pottery shards (see Appendix C for detailed information). The 3 obsidian flow samples consisted of fragments chipped from in-situ obsidian flows in Pachuca, Hidalgo, Mexico (abbreviated here PHM), Glass Buttes (also called Little Glass Buttes), Oregon, USA (LGB), and Long Valley Caldera, California, USA (LVC); these materials are categorized as "Other Reference Materials" (ORM's) in this study. The 8 geological and geochemical standards used in this study consisted of: 1) 6 international geological and geochemical standards, which served as "Primary Standards": United States Geological Survey (USGS) RGM-1, BCR-1 and BHVO-1; National Institute of Standards and Testing (NIST) SRM-278 and SRM-2709; and GSD-5 from China; and, 2) 2 USGS in-house (for use only within the USGS) geological and geochemical standards, which served as "Secondary Standards:" PPG and SJS. See Appendix B for more detailed information regarding the ORM's and Primary and Secondary Standards.

Sample Preparation

Preparation of all samples for analysis via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) involved 4 steps: 1) cleaning of the solid samples to remove surface contamination; 2) crushing of the solid samples to small fragments (~¼ to ½ in.) to facilitate pulverization; 3) pulverization of crushed & uncrushed solid fragments or pieces; and, 4) conversion of pulverized samples to liquid solutions using a 4-acid digestion process. The acid digestion step was necessary as the ICP-MS used in this study can perform analyses only on samples that are in liquid form. Pulverization of each solid sample was performed for 2 important reasons: 1) to increase the surface area of the sample, thereby increasing the ease and efficiency of its digestion into liquid form; and, 2) to facilitate the homogenization of each sample, thereby ensuring the resulting chemical analyses represent the compositions of the sample pieces in their entirety.

To ensure homogeneity of a rock, soil, or sediment sample, the desired particle size range is less than 200-mesh (see for example: Briggs and Meier 1999; Govindaraju 1984, 1994; Obenauf et al. 2000; Taylor 2001). A 200-mesh sieve (U.S. Standard Sieve No. 200) only allows particles with diameters ≤75 μm to pass through (Obenauf et al. 2000); this corresponds to particle sizes ranging from silt-size (2 to 75 μm) to clay-size (<2 μm). Seventy-five μm is small enough to ensure that any mineral grains present are sufficiently broken down to allow for their even distribution throughout the entire pulverized sample (Obenauf et al. 2000), thus every portion of the pulverized sample will have the same composition. Yet, this size is large enough that the aggregation of particles due to electrostatic attraction, with subsequent interference to homogenization of the particles, is minimal (Obenauf et al. 2000). Obsidian, being a rock, should theoretically be pulverized down to this size, however its inherent compositional homogeneity can allow for homogeneity of pulverized samples with somewhat larger particle sizes. All 100 obsidian debitage pieces and 3 ORM's were studied optically prior to crushing and pulverizing and found to be quite homogeneous (discussed later in this Appendix; descriptions of ORM's given in Appendix B and artifacts in Appendix C). Thus, this researcher was comfortable in not attaining strict pulverization of these materials down to ≤200-mesh in a number of cases, as discussed in the Sample Crushing and Sample Pulverization sections of this Appendix.

Sample Cleaning

All 100 debitage pieces and 3 ORM's were cleaned of fingerprints, soil, and labeling materials using ethyl alcohol, Kim-Wipes, and a new soft toothbrush. Ethyl alcohol was used as it does not interact chemically with the artifactual materials to a significant degree, and evaporates quickly leaving no residue. Kim-Wipes and the alcohol were used for light rubbing during removal of surface contamination. A number of debitage pieces also required light to moderate scrubbing using the alcohol and toothbrush, as detailed below.

All 96 obsidian pieces were observed to have "worked" and/or "unworked" surfaces, as termed here. "Worked" surfaces consisted of knapped or chipped surfaces, and were smooth, vitreous, conchoidally-fractured surfaces resulting from the deliberate chipping away of material by man to reveal fresh obsidian (or being the unwanted material that had been chipped off other pieces). None of these surfaces showed more than light weathering, with the most highly-weathered being only somewhat dullish (see Appendix C). Weathering of obsidian often results in a dull appearance, as the glass reacts with water or moisture, and the various chemical constituents carried by that water or moisture (see Chapter 2). "Unworked" surfaces consisted of unknapped or unchipped surfaces, had irregular contours, and were somewhat vitreous to somewhat dullish. These unworked surfaces are most likely original "outcrop" surfaces, remnants of the surface of the solidified obsidian from which the pieces had been broken. This type of surface is more accurately termed a cooling "crust," as it was produced on the outer surface of an obsidian flow as the hot lava met the cooler air (or sometimes water) and was cooled quickly (see Chapter 2). This crust, just as with fresh surfaces, also becomes weathered over time, as some of the pieces here appear to show (see Appendix C). The pieces of the 3 ORM's also had both worked and unworked surfaces (see Appendix B).

Soil was found to be ground into some surfaces, especially the irregular unworked (cooling crust) surfaces, thus necessitating light to moderate scrubbing using the soft toothbrush. Short soaking (~5 min.) of the more stubborn areas in ethyl alcohol was mostly to completely successful for all samples. It was not possible to remove all ground-in material from several debitage pieces, especially those with somewhat rough surfaces. Dr. Frederick Lange, the archaeologist who led the excavations during which the debitage pieces studied here were unearthed, and his assistants, had painted labels on them for archival and organizational purposes. These labels appeared to consist of a white background layer of White-Out, or Liquid Paper, with the assigned artifact number having been written on top of this surface with a black marker. These small, irregularly-to rectangularly-shaped labels (~3 mm x ~8 mm) were often hard to completely remove, and many required moderate scrubbing with the toothbrush. Small portions of the white backgrounds of labels could not be removed from 3 obsidian pieces (see Appendix C, Obsidian Artifacts section, and Figures C-6 and C-8).

During cleaning, several very small (≤1 mm) coppery to reddish-copper colored "droplets" were observed on 5 of the 96 obsidian debitage pieces, these being CS-01, CS-12, CS-23, CS-26, and CS-27. After the initial cleaning step in which the surface contamination and labels were removed, each of these 5 obsidian pieces were cut into 2 portions using a diamond saw. They were each cut so that the portion containing droplets would be as small as possible, and yet still retain all the droplets for further study. Thus, the "barren" obsidian-only portions of each were as large as possible, so the compositions of these portions would be as representative as possible of the entire debitage piece. Both portions of each of these 5 debitage pieces were placed in 5 beakers (both portions of one piece per beaker) along with a small amount of ethyl alcohol (~10 ml), with the beakers then placed in an ultrasonic bath partially filled with water and allowed to vibrate for ~15-20 minutes; this procedure was repeated, after cleaning the beakers and adding fresh ethyl alcohol to them. This extra cleaning step helped ensure that each portion of these 5 pieces were free of contaminants transferred to them during cutting with the diamond saw. At this point, 2 droplets were removed from the droplet-retaining portion of debitage piece CS-01 and mounted on thin sections for analysis via Electron Microprobe (EMP); see Chapter 6 for information regarding the droplets.

Sample Crushing

All 100 debitage pieces and 3 ORM's were cleaned a second time with ethyl alcohol and Kim-Wipes immediately prior to crushing, to remove any contamination due to handling since their first, thorough cleaning. Crushing of the pieces and ORM's was performed for two reasons: 1) it would serve to expedite the pulverization of these solid materials; and, 2) it should allow for the most accurate compositional information possible to be obtained for these materials, as it would allow for selection of fresh, unweathered pieces for analysis. However, for nearly all 100 of the artifacts, and for 2 of the 3 ORM's (PHM and LGB), this selection procedure either was not practicable, or was decided by this researcher to be unnecessary, as discussed below.

It was desirable to remove all the portions containing weathered surface crusts, weathered worked surfaces, and/or altered portions, yet leave as much of the artifact as possible; thus chemical analysis would yield the most accurate information regarding the entire artifacts' composition. However, satisfying both these competing requirements turned out to be virtually too difficult to attain, impossible, in fact, in many cases. After performing this procedure on the first few debitage pieces containing a weathered surface(s), it became clear that to continue the process left a significantly reduced amount (mass) of each debitage piece; the resulting masses of many debitage samples would be too small (or nearly so), to allow for their chemical analysis to be obtained, as a number of these pieces were quite small to begin with. For example, piece CS-03, composed of obsidian and with ~25% of its' surface being weathered, had a starting mass of 1.4409 g. After crushing and removing the portions containing weathering, there was less than ½ of this sample remaining, or ~0.6-0.7 g. The acid-digestion process requires a sample mass of 0.2 g ± 0.002 g; further, it was not known at this point how much sample loss could be expected during pulverization. In addition, if any ICP-MS analyses would need to be repeated, or if other chemical analyses were to be conducted, a much larger powdered sample mass than 0.2 g would be needed.

However, before abandoning this potentially critical process of removing crushed portions of debitage pieces including weathering, this researcher reviewed information regarding the weathering of obsidian (presented briefly in Chapter 2). The cooling crusts present on those obsidian debitage pieces which had them also did not appear similar to what would be expected when significant hydration has occurred, as most of these were not very dull. Even the thickest cooling crust did not appear to be especially thick (<~1 mm) when viewed in cross-section during the optical observations of the pieces, and most were much thinner than that. After having reviewed the information regarding expected depth of hydration over time (again, see Chapter 2), this researcher felt comfortable in not pursuing the additional procedure of removing crushed chunks of each obsidian debitage piece containing cooling crust or a weathered surface. It was decided that the benefit of retaining all of each debitage piece would outweigh the small degree of uncertainty involved in assuming that very little chemical change had occurred in the very outermost surface of the pieces, especially as compared to the entire mass of the entire piece.

The only sample of obsidian that was subjected to the procedure wherein the portions containing weathering were removed was the ORM LVC. Three moderately large pieces (~20 g each) of this obsidian were made available for use in this study, and all contained numerous largish portions (~1-2 in. in diameter) that were weathered and/or chemically altered. Because obtaining as representative an analysis as possible for this material in its fresh, unweathered state was of high importance, it was necessary to obtain only unweathered portions for analysis. All three pieces were broken into smaller chunks using a fairly new rock hammer that had been cleaned well using ethyl alcohol and a soft toothbrush. Great care was taken in selecting only fresh, unweathered, unaltered pieces for crushing, and portions from all 3 original pieces were selected.

The desired fragment size after crushing was ~¼ in. to ½ in., as fragments of this size fit nicely into the mixer/mill (pulverizer) vials, and left enough room in the vial for the inserted ball to move around, effectively pulverizing the fragmented material. Two separate sets of mortars and pestles were used for crushing the solid samples, with one composed of stainless steel and the other of agate. These were both cleaned well prior to use in this study, as well as between each use, to ensure little or no cross-contamination between samples. The agate mortar and pestle (together they comprise what is termed here the “agate unit”) is each composed of a solid piece of agate, light gray-brown in color and mostly opaque. As the composition of agate is essentially 100% SiO_2 (see for example: Best 2003; Hall 1996; Wilson 1989), it is expected that very little or no contamination would be introduced to samples crushed in this unit.

A stainless steel-plated brass mortar and a solid stainless steel pestle comprise the “stainless steel unit.” The mortar is composed of 3 separate pieces, the first of which is a thin (~⅜ in. thick), flat, square base ~3-in. long on each side. The second piece is a thick (~1 in. thick), round crushing surface ~2 ½ in. in diameter. A screw, coming up through the square base from its bottom, allows for very firm attachment of the round crushing surface on top of the base. The third piece, a thin (~⅜ in. thick) cylinder of moderate height (~4 in. tall), fits snugly down around the round crushing surface and is seated along its’ bottom edge onto the square base. The cylinder, when seated against the square base, attaches quite firmly to the round crushing surface by means of 3 wing screws, set ~120° apart, through the cylinder and against the round crushing surface. All 3 pieces comprising the stainless steel unit are composed of stainless steel-plated brass, and the crushing surface has been worn down in several places such that small portions of the brass underneath are revealed. Thus, contamination from both the stainless steel and the brass may be expected in samples crushed in this unit. The round crushing surface was so firmly attached to the square base that it was unnecessary to separate them for cleaning, although it was separated before the very first use in this project and cleaned well. These 2 pieces remained attached throughout their use thereafter during this study.

Both the stainless steel and the agate unit were cleaned using ethyl alcohol and a new test tube brush, with the brush vigorously applied to ensure cleanliness of all surfaces. Each piece was rinsed with a generous amount of ethyl alcohol and allowed to air dry. If any powder remained on either unit, ethyl alcohol and Kim-Wipes were used to rub this material off, and the brush and rinse re-applied, as many times as needed to completely remove any remaining residue. Both units were cleaned in this same manner, both before first use of each day, and after each sample.

The 3 ORM's and the larger debitage pieces (≥0.5 g) were crushed using the stainless steel unit to produce pieces having a maximum size of ~¼ in. Unfortunately, the agate unit, which was purchased specifically for this project, could not crush samples larger than ~0.5 g efficiently. Agate was the more desirable of the 2 units for use in this project, as its composition would significantly minimize contamination (see above) introduced to samples during crushing. However, the bowl of the mortar was quite shallow, and the sample pieces flew out as the pestle was applied to them, even in a gentle manner. This researcher experimented with a piece of cardboard (with a hole pierced through the middle of the cardboard and the pestle slipped through) covering the mortar to keep the pieces within the bowl while crushing. However, this was quickly abandoned as it was not only very difficult to determine what was going on within the mortar while the cardboard covered it, but it was also hard to maintain a firm hold on the mortar and cardboard with one hand while applying the pestle with the other.

Only 3 debitage pieces were small enough to be both crushed and pulverized successfully in the agate unit (those <0.2 g in mass), while 33 others were crushed in the stainless steel unit and then pulverized in the agate unit (those were ~0.2-0.6 g in mass). Another 3 had been crushed in the agate unit (those were ~0.7-1.4 g in mass) and then pulverized using the mixer/mill. Sixty one debitage pieces were too large to be crushed in the agate unit, so were crushed in the stainless steel unit. There was a noticeably increased retention of crushed pieces within the agate unit when even a small amount of ethyl alcohol (~2.5-5 ml) was added to the bowl of the mortar, which resulted in smaller losses of sample. And, the smaller the fragments, the better the liquid seemed to retain them in the mortar bowl.

The smallest debitage pieces (those <0.5 g in mass) were not completely pulverized to powder, as about one-quarter to one-eighth the volume of these samples remained as tiny (<0.5 mm), partially-pulverized fragments. The amount of time needed to completely pulverize these was found to be excessive, with little benefit thought to be gained, and attaining complete pulverization of these tiny fragments was abandoned after going through the process twice to see how long it would take. Because all of these very small debitage pieces were obsidian, a volcanic glass, any crystalline phases present should be extremely small; indeed, the obsidian debitage pieces and ORM's were observed using a microscope, and the microcrystals (microlites) present were quite tiny (see Appendix C, Table C-2, for artifact descriptions, and Appendix B, Other Reference Materials section for ORM descriptions). The tiny size of the minerals should not hamper their complete digestion during the acid digestion procedure, as the method has been developed specifically for use with crystalline rocks, which are typically much more difficult to digest than obsidian; to verify, each digestion vessel was observed after digestion, and in no case were any crystals or residues observed (see Sample Digestion section later in this Appendix).

After crushing each debitage piece or ORM sample, the broken portions plus small amount of powder was turned out onto a clean sheet of notebook paper using a microspatula. This sheet allowed for transferal of the crushed sample to a mixer/mill pulverizing vial, using the paper like a funnel. A new sheet was used for each debitage piece or ORM, and this sheet was reserved for later use when transferring the same powdered piece or ORM to its' sample vial. Because the cylinder and the round crushing surface of the stainless steel mortar unit are designed to be separated and reattached repeatedly, there is a very small gap between them. This gap tended to entrain tiny shards of a crushed sample, thus simply turning the mortar upside-down to dump out the crushed sample was insufficient. The cylinder was fully removed from the round crushing surface (with the round crushing surface still attached to the square base, as described earlier) after each sample was crushed. Both the square base and the cylinder were each struck lightly 2-3 times to jar loose any pieces of the sample stuck to their surfaces. As the round crushing surface was very firmly attached to the square base, there was no gap between. When cleaning the entire unit after a sample, as much of this join as could be reached was cleaned very well, thus cross-contamination between samples is unlikely.

Sample Pulverization

A SPEX 8000M-115 CertiPrep Mixer/Mill unit, housed in the Chemistry and Geochemistry Department, Colorado School of Mines (CSM), Golden, Colorado, USA, was used for pulverizing the 100 debitage pieces and 3 ORM's. An 8011 Multiple Sample Adapter, which holds 4 mixer/mill vials, was used so 4 samples could be pulverized simultaneously. Each mixer/mill 3127 Hardened Tool Steel Vial Set, made of "Worpliss" tool steel, consisted of a ¾-in. diameter x 1 ⅞-in. long hollow cylinder (capable of holding a grinding load of 0.5–1.0 ml, or 0.5 g of material, or a mixing load of 2 ml), 2 removable end caps, and a ¼-in. diameter steel ball (Obenauf et al. 2000). A Cole-Palmer Ultrasonic Cleaner, model #8845-2, also housed in the Chemistry and Geochemistry Dept., CSM, was used for cleaning the mixer/mill vials and crushing balls.

Only 4 mixer/mill vials were used in this study, with each vial being composed of a cylinder, 2 end caps, and a crushing ball. Two of the mixer/mill vials used here had been purchased specifically for this project, and the other 2 had been purchased for and used in only one previous project with samples of somewhat similar chemistry, petrified wood (Rowsey 2001). Before first use in this current project, each vial (every piece comprising one vial) was placed in a 100-ml glass beaker ~one-third full of ethyl alcohol, the beaker placed in the ultrasonic cleaner, and allowed to vibrate for 30-35 minutes. Each piece was separately rinsed with ethyl alcohol and wiped with Kim-Wipes, the ethyl alcohol in the beaker replaced, and the process repeated. Each of the 4 vials had numbers etched onto its' cylinder and both end caps, which made for accurate reconstruction of each vial after cleaning, save the crushing balls.

All 4 vials were cleaned extremely well before first use of the day, and after each sample had been pulverized. This cleaning step was achieved by placing 2 complete, but disassembled, vials inside each of two 100-ml beakers filled ~one-half full with ethyl alcohol, the beakers placed inside the ultrasonic cleaner, and allowed to vibrate for 10 minutes. The vibration served to agitate the ethyl alcohol, and vial pieces, aiding in removal of powder from the vial pieces. The ethyl alcohol in each beaker was replaced after each cleaning. If any powder remained on a vial, it was wiped thoroughly with a Kim-Wipe wetted with ethyl alcohol and then re-vibrated with the ultrasonic treatment. After the ultrasonic treatment, each piece of each vial was carefully rinsed with ethyl alcohol and allowed to air dry. The microspatula and tweezers were carefully cleaned using ethyl alcohol and Kim-Wipes after each use.

The manufacturer of the vials, SPEX, indicated that the vials will hold 2-10 g each and that this amount of material will be pulverized such that 85% will pass 200-mesh (the desired particle size) in 8-15 min. (Obenauf et al. 2000). However, it was not indicated how long it would take for 100% of the sample to become pulverized to that size. This researcher found that when the vials were loaded with samples larger than ~2 ½ g, they did not reach a homogeneously pulverized state after as long as 40 minutes. Numerous small (≤1 mm) fragments remained, and a significant amount of the well-powdered portion of the sample became tightly packed onto the inner walls of the vial, onto the surface of the ball, and into the end caps. These tightly-packed portions were difficult to remove from the various vial surfaces, and even after a moderate amount of scraping using a microspatula, a significant amount of material could not be recovered. Scraping of the material off the vial surfaces may have resulted in increased contamination to these samples. This tightly-packed powdered portion had to be repeatedly smashed down on its' paper with a microspatula to separate the hard, tightly-packed material, to find the unpulverized pieces, and to ensure homogenization of the sample powder. When removing these overloaded(?) vials from the mixer/mill, it was observed that the end caps had often been pushed outward from the ends of the vial cylinders, ~½ mm, up to 1 mm. Because the end caps overlap the cylinder ends on both sides by ~2-3 mm, loss of sample was unlikely. The end caps being pushed outward may have occurred due to increased outward pressure from the tightly-packed sample inside. The manufacturer may be describing this very situation: "When samples agglomerate or 'cake' during grinding, further particle size reduction is clearly inhibited. Caking can result from … the fusing of particles under pressure" (Obenauf et al. 2000).

Perfectly pulverized samples poured out of their vials easily, with little powder retained on the inner vial surfaces or ball; little or no scraping of vial surfaces was necessary for these samples. The tiny, unpulverized pieces from the overloaded vials described earlier would not completely pulverize if the entire sample was re-loaded into the vial and sent through another cycle. The exact same situation would recur, with part of the powder becoming tightly-packed, effectively shielding any remaining fragments from the crushing action of the ball. However, if the unpulverized pieces were picked out of the powdered portion and loaded into the vial and re-pulverized, these fragments would pulverize. Yet, other than going through this separation and re-pulverization process to ensure that full pulverization of a sample would indeed occur, this was not performed regularly; it took an inordinate amount of time to unload the vial, scrape out the tightly-packed powder, smash it down, locate the unpulverized fragments, load them into the vial, and put them through another cycle. Therefore, to increase pulverization efficiency, and especially to minimize sample loss, pulverization time, and sample contamination, the mass of crushed sample loaded into a vial was kept at ~2 g; there were no problems encountered thereafter when the mass was kept close to this size.

Four debitage pieces were composed of materials other than obsidian, and thus required somewhat different treatment. The first 2 of these samples were pottery shards (UNI-07 and UNI-08), which were much softer and less dense than obsidian; due to their fairly large size, they were crushed using the stainless steel unit. These samples were not pulverized in the mixer/mill, as their softness may have resulted in much of their powders becoming packed onto the inner surfaces of the vials (similar to that described above for overloaded vials), thus possibly leading to excessive sample loss and/or contamination; the crushed pottery shard samples were pulverized in the agate unit. As a distinct residue remained in the agate unit after pulverizing the first of these samples, a very small (~0.5-1 g) piece of LVC (leftover from breaking up the 3 large LVC pieces to eliminate the altered portions, as discussed earlier) was crushed and pulverized in the unit to clean it; this step was repeated with a second piece of LVC, to doubly ensure removal of contamination from the unit. This cleaning procedure was repeated after pulverizing the second of these samples as well. The other 2 non-obsidian debitage pieces were a quartz pebble (UNI-05) and a long, thin blade of silicified conglomerate (UNI-06). As both these materials are significantly harder than obsidian, both these pieces were crushed in the stainless steel unit. It was anticipated that the greater hardness of these materials would necessitate a longer pulverization time than that of obsidian, and thus were crushed into smaller pieces (≤1/16 in.) than the obsidian had been (≤1/4 in.), and even with these smaller-sized crushed fragments, both these debitage pieces took ~one-quarter to one-half again as long to completely pulverize as obsidian samples of similar mass.

Only 3 obsidian debitage pieces were small enough to be both crushed and pulverized successfully in the agate unit, and these were all <0.2 g in mass; these are expected to have had virtually no contamination introduced into them, as the agate is almost entirely SiO_2. Another 3 obsidian debitage pieces had been crushed in the agate unit (these were ~0.7-1.4 g in mass) and then pulverized in the mixer/mill vials; these are expected to have the next least amount of contamination, with these sources being the agate (again, not anticipated to contribute significantly) and the tool steel of which the mixer/mill vials and balls are composed. Thirty three obsidian debitage pieces, and the 2 pottery shards, were crushed in the stainless steel unit and then pulverized in the agate unit (these were all ~0.2-0.6 g in mass); these are also expected to have a somewhat low amount of contamination, with the contamination sources being both stainless steel and agate. The remaining 57 obsidian debitage pieces, and the other 2 non-obsidian debitage pieces (the quartz pebble and the blade of silicified conglomerate), were crushed in the stainless steel unit and then pulverized in the mixer/mill vials; these are anticipated to have the most contamination, with the sources being the stainless steel and the tool steel. The contamination introduced by the mixer/mill vials during pulverization is anticipated to consist of minor amounts of Fe, and very minor amounts of Cr, Si, Mn, and C (Obenauf et al. 2000).

Once a sample was completely pulverized, the powder was dumped out of the vial, or the agate unit, onto the same piece of paper that had been used to transfer the crushed sample to the pulverizing unit (as stated earlier). Any powder that was retained on the mixer/mill vial (walls, end caps, and ball) or surfaces of the agate unit was lightly scraped off using a microspatula onto the paper. If necessary, the crushing ball was held with tweezers while material was scraped off of it. The powdered sample was then transferred to a plastic sample vial using the paper as a funnel. A number of samples were large enough that they required several portions to be pulverized separately. To minimize sample loss and potential contamination for these larger samples, the same mixer/mill vial(s) and sheet(s) of paper were re-used for successive portions of the same sample, with the mixer/mill vial(s) remaining uncleaned between successive loads. If a debitage piece or ORM sample required more than one portion to be pulverized, each successive load of powder was piled onto the other(s) on its paper. After each sample was completely pulverized, whether in one load or several, it was homogenized as completely as possible without introducing much further contamination. This was accomplished by both mixing the pile of powder using a microspatula, and by folding the powder over itself by rolling the paper in several directions for several minutes. This process was done to produce as homogeneous a powder as possible before transferring it to the sample vial. A homogeneous powder in each sample vial was necessary before moving the powdered samples to the facility where the chemical analyses were performed; the ability, and time required, to homogenize the sample vial contents was unavailable at the facility, thus having them as homogeneous as possible before arrival was essential.

Sample Digestion

The analytical instrument used in this study, Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), can only analyze samples in liquid form, thus dissolution, or digestion, of the powdered solid samples into liquid form was necessary for analysis. The powdered samples involved in this study (100 artifacts, 6 Primary Standards, 2 Secondary Standards, and 3 ORM's) were digested using the method discussed below. Complete digestion of samples was of utmost importance, as any undigested material would yield low elemental values for that material. Crystals commonly found in obsidian include magnetite, titanite (sphene), and zircon (Bouška 1993), all of which can be difficult to digest. The acid digestion process used here has been developed and refined over many years, and is used mainly for digesting crystallized igneous rocks (Allen Meier, verbal communication 1/12/1999), which are usually more difficult to completely digest than glassy rocks, thus complete digestion of powdered obsidian was expected. Visual inspection of all 50 Teflon sample digestion containers, or vessels, was conducted using a 40x plane light binocular microscope (housed at the USGS) after each of the 3 digestion runs; no undigested residues, grains or crystals were observed in any case.

The reader is referred to Briggs and Meier (1999) for the following discussion. An important benefit for using the 4-acid digestion process used here is that of removing silicon (Si), which makes up the largest portion of each obsidian sample by weight ($\geq 70\%$). Silicon forms a complex with fluorine (F) from the hydrofluoric acid in the digestion procedure, and this complex (SiF_4) becomes volatilized during the digestion process. Removal of Si serves to concentrate the remaining elements in the sample aliquots, which is especially important for elements present in trace amounts, such as many of the elements studied here. The concentrations of these elements in the final aliquots should then be greater than their instrumental detection limits, making them easier to detect and measure, thereby increasing the precision, accuracy, and confidence of the measurements. However, the dilution factor by the end of the digestion process is 1:500, or 1 g of rock per 500 ml of digestion aliquot. Thus, by starting with a sample size of 0.200 g of rock powder (as is done here), the ending liquid, or aliquot, at the end of digestion has 0.002 g of rock per 1.0 ml of liquid. This dilution is necessary in order to minimize build-up of salts and other particles within the instrument, which decreases its efficiency and sensitivity. Therefore, the measurement precision, accuracy, and confidence are dependent on the 2 opposing factors of concentration and dilution.

The powdered samples (debitage pieces and reference materials) analyzed here were digested following the procedure used routinely by Allen Meier, Research Chemist with the Crustal Imaging and Characterization Team, Geologic Division, USGS, which is the Multi-Acid Digestion Method (Table A-1). This procedure utilizes a combination of 4 acids to digest the samples. Lutetium (Lu) serves as an internal standard, or “spike,” in this methodology, and was chosen for 2 reasons: 1) although Lu may be present in small amounts in a given sample, it is not usually requested in chemical analyses of rocks; and,

Table A-1. Multi-Acid Digestion Method.

1. Select appropriate number of Teflon vessels; be sure to include samples, duplicate samples, standards, and 3 reagent blanks.
2. Weigh 0.200 g of samples into each vessel.
3. Add 100 µl of Lu spike (internal standard) to each vessel.
4. Rinse sample from inside walls down to bottom using minimum amount of deionized water (DI).
5. Add 3.0 ml of concentrated hydrochloric acid slowly.
6. Add 2.0 ml of concentrated nitric acid, and allow any reaction to subside.
7. Add 1.0 ml of concentrated perchloric acid, followed by 2.0 ml of concentrated hydrofluoric acid.
8. Place vessels on aluminum heating block set to 110°C, and heat to incipient dryness (overnight).
9. Remove vessels, rinse down inside walls with minimum of DI, and add 1 ml of perchloric acid. Increase heat of block to 160°C, and replace vessels on block. Take to final dryness (overnight).
10. Remove vessels from heating block, add 1.0 ml concentrated ultrapure nitric acid, and add 2 drops of hydrogen peroxide (samples high in Mn may require more peroxide). Let reaction subside.
11. Add 9.0 ml 1% nitric acid to each vessel, cap tightly and shake. Place in 100°C warming oven for 1 hour. Remove vessels and let cool. (Samples diluted in this step to 1:50—0.2 g into 10 ml solution)
12. Take 0.50 ml aliquot from each vessel and dilute to 5.0 ml with 1% nitric acid as final preparatory step for analysis by ICP-MS. Place diluted samples in polypropylene test tubes with caps until ready for analysis. (Samples diluted in this step to 1:10; overall dilution is now 1:500—0.2 g into 500 ml solution)
13. Wash vessels and caps with soapy water and bottle brush. Rinse 3 times in tap water, then 3 times in DI water. (If very dirty, soak overnight in 1% nitric acid and then rinse in DI water).

Reagents used:

Hydrochloric acid (HCl), concentrated reagent grade (37%)
Nitric acid (HNO_3), concentrated reagent grade, or ULTREX grade (70%)
Perchloric acid ($HClO_4$), concentrated reagent grade (70%)
Hydrofluoric acid (HF), concentrated reagent grade (48%)
Hydrogen peroxide (H_2O_2), solution (30%)
1% Nitric acid: Dilute 10.0 ml concentrated HNO_3 to 1000.0 ml with deionized water

Reference:

Briggs, Paul H., and Allen L. Meier. 1999. *The Determination of Forty Two Elements in Geological Materials by Inductively Coupled Plasma-Mass Spectrometry*. Open-File Report No. 99-166. United States Government Printing Office, Washington, DC. 15 p.

2) Lu is a relatively problem-free element to analyze (Allen Meier, verbal communication 1/12/1999). Internal standards are difficult and time-consuming to test and properly develop, and Lu is nearly ideal for the above reasons.

The digestion process took place in 50 small (~100 ml), white, Teflon digestion vessels, also called "bombs," with screw-on caps. Before each of the 3 digestion "runs" involved in this study, the 50 Teflon vessels and caps underwent a rigorous cleaning procedure, which consisted of being soaked overnight in nitric acid (1%), scrubbed out well with a new bottle brush and mild dish soap, rinsed thoroughly with tap water, rinsed 3 times with generous amounts of de-ionized water (DI water), and air-dried overnight; this cleaning procedure was repeated after each use as well. Each digestion run uses a maximum of 50 Teflon digestion vessels, with one digestion run constituting one analytical run. Allen Meier, USGS (verbal communication 1/12/1999), routinely includes in every digestion run 3 blanks, 2 USGS Secondary Standards, and a minimum of 4 other standards, with his choices for the latter based on the anticipated compositions of the samples to be analyzed. As the compositional range here was unknown, especially for the non-obsidian pieces, his selection for the 4 other standards covered a fairly wide range: 2 moderately felsic standards (GSD-5, a stream/pond sediment, and SRM-2709, an agricultural soil), and 2 mafic standards (BCR-1 and BHVO-1, both basalts). This project primarily involved obsidian, which is often felsic to intermediate, thus this author also included the 2 international obsidian standards (RGM-1 and SRM-278).

Three digestion runs (and thus 3 analytical runs) were needed to obtain analyses for all 100 debitage samples and 3 ORM's. In addition to the 3 blanks, 6 Primary Standards, and 1 or 2 of the Secondary Standards mentioned above, each of the 3 digestion/analytical runs also included all 3 ORM's and 33 or 34 artifact samples. This left room for addition of 3 duplicated samples (a second portion of the same sample, subjected to an entirely separate digestion) per digestion/analytical run (see Appendix B, Sample Duplicates section). The first 2 digestion/analytical runs each contained all 6 Primary Standards, the 2 Secondary Standards, and 33 artifact samples. The third run contained all 6 Primary Standards, only 1 of the 2 Secondary Standards, and 34 debitage samples; one of the Secondary Standards was eliminated to make room for the remaining 34 debitage samples, and still have room for 3 duplicated samples.

All 6 Primary Standards and both Secondary Standards were obtained from their respective organizations in powdered form, with the Primary Standards contained in glass bottles and the Secondary Standards in Teflon bottles, thus cleaning, crushing, and pulverizing were unnecessary for these materials. However, these powders had been sitting for an unknown amount of time, and some differential settling of the powdered material had likely occurred. The jars were shaken vigorously for several minutes, in both up-and-down and side-to-side motions, to re-homogenize the contents. In addition, the 2 Secondary Standards each contained partially incompletely-pulverized material, with a somewhat large range of particle sizes (see Appendix B, Secondary Standards section). Thus, these 2 materials yielded analytical results having a more varied and less well-constrained, compositional range than that of the homogeneously powdered reference materials (see Appendix B, Tables B-3 through B-30). Aside from re-pulverizing the entire contents of each of these bottles, there was no way to significantly improve the homogeneity of these 2 materials.

Small portions (0.5-1.0 g) of each reference material were removed from each of their respective jars and placed on separate, clean watch glasses, and heated in a ~100^{o}F drying oven for ~1 hour. This was done to drive off any moisture that had been adsorbed onto the particles during storage in the bottles, thus ensuring that only rock powder would be included in the analyses. After being allowed to cool to room temperature, these portions were each turned out onto clean sheets of notebook paper and homogenized similar to that described in the Sample Pulverization section of this Appendix. Samples of the appropriate mass (0.2 g ± 0.002 g) were then weighed out from these prepared portions and digested according to the procedure given in Table A-1.

ICP-MS Methodology

Explanation regarding how an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) instrument works, how it is operated, and how the raw data from the instrument is interpreted into useful compositional data is beyond the scope of this work; the reader is referred to such excellent texts as the following for such information: Jarvis et al. (1992); Johnstone and Rose (1996); Taylor (2001); and Watson (1997). Other information common to all ICP-MS software and instruments, such as isotopes measured, and interferences, can also be found in these texts. Information regarding elemental detection limits, operating parameters, calibration standards and internal standards for the particular instrument and methodology used in this current study can be found in Briggs and Meier (1999). The published lower limits of determination (LLD), or detection limits, for elemental analysis of geological materials via the very same Elan 6000 ICP-MS used in this study (housed at the USGS, Denver Federal Center, Colorado) were obtained from Briggs and Meier (1999), and are listed in Table A-2. Although these published LLD usually represent the very best that a particular instrument is capable of detecting, the actual LLD for the instrument for a given analytical run may vary, for better or worse. Also listed in Table A-2 are the LLD for a number of elements as actually obtained during this study, some of which are lower (better) than published; the actual LLD obtained during the analyses performed here were, at times, better than those previously published. All of the LLD data presented in Table A-2 are reported in parts per million (ppm) in the rock, or rock concentrations, as explained below.

The compositional measurements presented in this study were obtained from the instrument operator, Allen Meier, USGS, post-interpretation and post-correction (Allen Meier, verbal communication 4/22/1999), and the following is a brief summary of the methodology he follows. The instrumental software had been designed to automatically take into account interference effects, and sample masses, to calculate the background threshold via the reagent blanks, etc., to interpret the raw instrumental response data into raw compositional information. Further adjustments are then made, "correcting" the raw compositional information, via comparison to compositional information for several standard materials; those used as comparisons for the 3 analytical runs of this study are: SRM-2709, GSD-5, SJS, and PPG. And finally, this "corrected" data was then "back calculated" into rock concentrations, which are element concentrations within the solid or powdered reference materials and standards, and solid artifacts, just as if they had been measured directly in those forms. As mentioned, Table A-2 lists the LLD for the ICP-MS in rock concentrations, and additionally, Tables B-2 through B-30 (Appendix B), and C-1 (Appendix C), list compositional data for the standards and artifacts, in rock concentrations. Please see Briggs and Meier (1999) for the actual mechanics regarding calculating rock concentrations from corrected compositional data.

Table A-2. Lower Limits of Determination (LLD) in ppm for Elemental Analysis of Geological Materials Via the Elan 6000 Inductively-Coupled Plasma Mass Spectrometer (ICP-MS).

Element	Reported Value, ppm *	This Study, ppm **
Ag	0.5	0.02
Al	50	*n/a*
As	1.0	0.5
Au	1.0	0.05
Ba	1.0	*n/a*
Be	0.1	0.1
Bi	1.0	ND
Ca	50	500
Cd	0.1	0.1
Ce	1.0	*n/a*
Co	1.0	0.1
Cr	1.0	1.0
Cs	--	0.1
Cu	1.0	3.0
Eu	1.0	ND
Fe	50	100
Ga	1.0	*n/a*
Ge	--	0.1
Ho	1.0	ND
In	--	0.1
K	50	*n/a*
La	1.0	*n/a*
Li	1.0	0.5
Mg	50	100
Mn	4.0	*n/a*
Mo	0.5	0.1
Na	50	*n/a*
Nb	4.0	*n/a*
Nd	1.0	ND
Ni	2.0	0.1
P	50	100
Pb	1.0	0.1
Rb	--	*n/a*
Sb	0.1	0.1
Sc	2.0	0.5
Se	--	1.0
Sn	1.0	ND
Sr	2.0	*n/a*
Ta	1.0	0.1
Te	--	0.1
Th	1.0	0.05
Ti	50	ND
Tl	1.0	0.1
U	0.1	0.05
V	2.0	1.0
W	--	0.1
Y	1.0	*n/a*
Yb	1.0	ND
Zn	2.0	3.0

* "Reported Values" are LLD values after Briggs and Meier (1999), and reported here in ppm.
-- Elements for which LLD values are not reported in Briggs and Meier (1999).

** "This Study" values are LLD values as obtained during this study, in ppm.
n/a = Elements for which LLD information from this study are not available.
ND = Elements not determined in this study.

Other Analytical Work

Before obtaining chemical analyses of the 100 debitage pieces and 3 ORM's via ICP-MS, these samples were first studied using a plane light binocular microscope (capable of up to 40x magnification), housed in the Chemistry and Geochemistry Department, CSM, and a 10x magnification hand lens, owned by this researcher. At least one thin section was prepared from each of the 3 ORM's, and these were studied using another binocular microscope, with both plane and cross polarized light at up to 800x magnification, housed in the Geology and Geological Engineering Department, CSM.

Optical Studies

Two types of optical studies were performed here upon all 100 debitage pieces and all 3 ORM's. The objectives of both optical studies were two-fold, the first being to identify any resistant phases (minerals known to be hard to break down, even using the four-acid digestion procedure used here) within these samples. Early identification of such characteristics that might pose a problem for accurate chemical analysis due to incomplete sample homogenization and/or digestion is essential. The second objective was to identify any discernable structures (banding, orientation of phenocrysts, weathering nuclei, etc.) within the samples, as physical structures may also deter complete homogenization and/or digestion of the material. Additionally, identification of these types of characteristics (resistant minerals, physical structures) within a given piece of obsidian may also aid in more fully characterizing the material. This, in turn, may also aid in identifying the source obsidian flow from which it was removed, thereby possibly aiding in the sourcing process in later studies (see Chapter 4).

The first optical study involved observing and recording the external and internal (as much as could be observed) physical characteristics of all 100 debitage pieces and 3 ORM's in their solid forms, prior to crushing. Many of the pieces of obsidian (debitage pieces and ORM's) were mostly translucent, and some portions were nearly transparent, thus all 96 obsidian debitage pieces, and 3 ORM's yielded much internal information. These external and internal physical observations were performed using a plane polarized light binocular microscope housed in the Chemistry and Geochemistry Department, CSM, at up to 40x magnification, and a 10x magnification hand lens owned by this researcher. See Appendix C, Table C-2, for more complete descriptions of all 100 debitage pieces, and Appendix B, Other Reference Materials section, regarding the 3 ORM's.

The 100 debitage pieces were observed in the solid forms in which they were received by this authors' Thesis Advisor, Dr. E. Craig Simmons, Department of Chemistry and Geochemistry, CSM, from the archaeologist who had excavated them, Dr. Frederick Lange, formerly with the University of Colorado at Boulder (see Appendix C). Also observed in their solid forms, were the ORM's PHM and LGB, both as received from Dr. Michael Glascock, with the Missouri University Research Reactor (MURR), University of Missouri, Columbia, Missouri; the ORM LVC was also observed in its' solid form, as received from Dr. Ronald Klusman, Department of Chemistry and Geochemistry, CSM (see Appendix B, Other Reference Materials section). As noted earlier in this Appendix, all 3 pieces of LVC were broken into smaller pieces using a rock hammer; these thinner pieces were also observed, to get more internal information.

The second type of optical study involved observation of the characteristics of a given ORM sample from at least one thin section prepared from that material. Thin sections of all 3 ORM's were kindly prepared by John Skok, Department of Geology and Geological Engineering, CSM. Only one thin section was prepared from each of the PHM and LGB samples, as these pieces were quite small and it was more desirable to retain as much of each as possible for chemical analysis. Each of the 3 pieces of LVC originally obtained from Dr. Ronald Klusman, CSM, contained weathered and/or altered portions (mentioned earlier), thus great care was taken to obtain thin sections from fresh, unaltered portions. Three thin sections were prepared from the largest LVC piece, each from a different area. All 3 of the original pieces of LVC were later broken into smaller chunks, and its chemical composition determined as described earlier in this Appendix. The thin sections of the 3 ORM's were studied using a different binocular microscope than that used earlier, this one housed in the Geology and Geological Engineering Department, CSM, and capable of magnification up to 800x in both plane polarized and cross polarized light (see Appendix B, Other Reference Materials section). Because only 5 or obsidian debitage pieces were large enough to yield thin sections, this researcher decided not to have thin sections prepared from any; thin sections would probably not yield much more information than that already obtained via microscope and hand lens, and it was of utmost importance to retain as much of each of these samples as possible for chemical analysis.

APPENDIX B
ANALYTICAL STANDARDS

This Appendix discusses the 11 standards and reference materials used in the analytical portion of this project and why they were chosen, as well as some basic information regarding the accuracy and precision of the analytical measurements obtained during this study. The reference materials were initially grouped into 3 classes based upon how well-known their compositions were. This initial classification (seen in Table B-1) served to identify between those reference materials that would be useful during the acquisition of the chemical analyses during this study ("Primary Standards" and "Secondary Standards"), and those that were included in this study for the main purpose of gaining more information about them ("Other Reference Materials"). This classification was later modified into 3 different groupings, based also on how well-known its composition, but mostly upon the overall composition of the material, as discussed in the Accuracy section of this Appendix. This later classification (seen in Tables B-3 through B-30, at the end of this Appendix), served the main purpose of separating the reference materials composed of obsidian ("Critical Standards" and "Supplemental Standards") from those composed of other lithic materials ("Additional Standards"), and was used for evaluating the accuracy and precision of the chemical data.

Factors for Choosing Reference Materials

The particular standards and reference materials used in analysis are usually chosen primarily on the basis of composition, and that was the main criteria for this project. Other factors might include the composition of the matrix, or chemical medium, in which the material was prepared and now resides, the actual behavior of the material due to the conditions achieved during chemical analysis, the precision with which the composition of the material is known, etc. An ICP-MS (see Appendix A) was the analytical instrumentation used in this study, and it is very sensitive to the matrix in which the sample is introduced. As explanation of the operation and use of ICP-MS is beyond the scope of this project, the reader is referred to such excellent texts as Jarvis et al. (1992), Johnstone and Rose (1996), Taylor (2001), and Watson (1997).

Of the 100 artifacts (debitage pieces) studied here, 96 were composed of obsidian, with the remaining 4 being comprised of 2 pottery shards, 1 quartz pebble, and 1 blade of silicified conglomerate. As the vast majority of these pieces, 96 out of 100, or 96%, is comprised of obsidian, the main material of interest here is obsidian; indeed, the ultimate goal for this study is determination of provenance (origin of materials) for the 96 obsidian debitage pieces. Using standards and reference materials composed of obsidian was therefore of utmost importance for eliminating matrix effects between the obsidian reference materials and obsidian artifact samples. For this reason, the only 2 obsidian standards known to exist at the time, RGM-1 and SRM-278, were both used in this study, as discussed below; the other reference materials chosen are also discussed below. A secondary criteria determining the selection of standards and reference materials was how well-known were the compositions of these materials. However, as this was of lesser significance, how it affected the selections are discussed to a lesser degree.

Reference Materials Chosen for This Study

Allen Meier, Research Chemist with the Crustal Imaging and Characterization Team, Geologic Division, Department of the Interior, USGS, Lakewood, Colorado, operated the ICP-MS used to obtain the chemical analyses of the samples presented here. As briefly discussed in Appendix A (ICP-MS Methodology section), he typically adjusts the raw analytical data according to set procedures; the reader is referred to Briggs and Meier (1999) for more information. Further, he compares newly-obtained analyses of several standards he works with regularly (such as SRM-2709 and GSD-5) to their known compositions, using these for internal calibration (Allen Meier, verbal communication 1/12/1999); all 3 analytical runs performed here included at least 10 of the 11 chosen standards and reference materials, so each run could be assessed properly (see Analytical Runs section of this Appendix).

Each ICP-MS analytical run included 3 blanks, both USGS in-house standards, SJS (an agricultural soil) and PPG (a granite), and a minimum of 4 other standards, with choices for the latter based on the anticipated compositions of the samples to be analyzed (Allen Meier, verbal communication 1/12/1999). Because the material of interest here is obsidian, it was vital to use as many obsidian reference materials as possible; the only 2 obsidian standards known at the time, SRM-278 and RGM-1, were included. Although "obsidian" (a natural glass) is usually felsic to intermediate, it can be of any composition (see Chapter 2). As these 2 standards are both fairly felsic, Allen thus chose to include 4 more standards to more fully cover the wide compositional range the artifacts might possibly encompass (Allen Meier, verbal communication 1/12/1999). Two standards of felsic to intermediate composition were included: GSD-5 (a stream/pond sediment), and SRM-2709 (an agricultural soil); the other 2 standards he selected were of mafic composition: BCR-1 and BHVO-1 (both basalts). Four artifacts studied here were not composed of obsidian, thus their compositions could only be roughly anticipated. Two of these, UNI-05 (a quartz pebble) and UNI-06 (a blade of silicified conglomerate), were composed of felsic, or roughly so, materials, thus their compositions were anticipated to fall within the compositional range represented by the felsic to intermediate standards. The compositions of artifacts UNI-07 and UNI-08 (both pottery shards) were entirely unknown, but should fall within, or at least near, the compositional range represented by all of the standards selected (see Appendix C, Table C-1, for artifact compositional data).

Primary Standards

Under the initial classification used here, the term "Primary Standard" is used for each of the 6 International Standard Reference Materials (SRM's) included here. This type of SRM consists of material whose composition has been analyzed so many times that it is well-characterized, or well-constrained (Govindaraju 1984, 1994). The 6 SRM's used in this project are geological and geochemical reference materials, and location and other information for these are given in Table B-1. These materials include: 2 obsidians (National Institute of Standards and Technology (NIST) SRM- 278, obsidian from Newberry Crater, Oregon, USA, and USGS RGM-1, rhyolitic obsidian from Glass Mountain, California, USA), 2 basalts (USGS BCR-1, basalt from Columbia River Group, Washington, USA, and BHVO-1, basalt from Kilauea Crater, Hawaii, USA), 1 agricultural soil (NIST SRM-2709, an agricultural soil from San Joaquin, California, USA), and 1 stream/pond sediment (GSD-5, a sediment, downstream from an area containing both diorite and carbonate rock, and copper skarns, Anhui Province, China). See also Tables B-3 through B-30, at the end of this Appendix.

Table B-1. Standards and Reference Materials Used in This Study.

Designation	Description & Location	References
Primary Standards -- International Standard Reference Materials *		
SRM-278	NIST (formerly NBS) “Obsidian Rock,” from Clear Lake, Newberry Crater, Oregon; Bottle # 291905.	Glascock et al. (1988); Govindaraju (1994); NIST Certificate of Analysis (1992).
RGM-1	USGS “Glass Mountain Rhyolite,” from Glass Mountain, Siskiyou County, California; 41°37' N latitude / 121°29' W longitude; Bottle: Split 44, Position 10.	Govindaraju (1994); USGS Certificate of Analysis (1995).
BCR-1	USGS “Analyzed Basalt,” from Columbia River Group, Bridal Veil Flow Quarry, Washington; NW 1/4 of SW 1/4, Sect. 14, T1N, R5E; Bottle: Split 7, Position 20.	Govindaraju (1994).
BHVO-1	USGS “Hawaiian Basalt,” from Kilauea Crater, Hawaii; 19°25' N latitude / 155°17'30" W longitude; Bottle: Split 15, Position 12.	Govindaraju (1994); USGS Certificate of Analysis (1995).
SRM-2709	NIST (formerly NBS) “Agricultural Soil,” from San Joaquin Valley, California; 120°15' N latitude / 36°30' W longitude; No bottle #.	Govindaraju (1994); NIST Certificate of Analysis (1993).
GSD-5	“Geochemical Reference Sample,” a stream / pond sediment from diorite / carbonate rock / copper skarn area in Anhui Province, China; Bottle #124513.	Govindaraju (1994); Xie et al. (1985).
Secondary Standards -- USGS In-House Standards **		
PPG	“Pike’s Peak Granite," from Colorado; No bottle #.	USGS (undated).
SJS	“San Joaquin Soil,” from San Joaquin Valley, California; No bottle #.	USGS (undated).
Other Reference Materials ***		
PHM	Obsidian from Pachuca (also called Sierra de Pachuca, Sierra de las Navajas, and other names), Hidalgo, Mexico; ~20°06 N lat. / between 98°25' - 98°45' W long.	Glascock (1999).
LGB	Obsidian from Little Glass Buttes (also called Glass Buttes), Lake County, Oregon; 43°31'23" N latitude / 119°59'21" W longitude.	Glascock (1999).
LVC	Obsidian from Long Valley Caldera, California.	n/a

* SRM's obtained in powdered form. Analytical sample taken after entire bottle contents homogenized.

** In-house standards obtained in powdered form. Analytical sample taken after homogenization of heterogeneous bottle contents attempted. See text for explanation.

*** Other reference materials obtained in solid form. Analytical sample taken after entire piece(s) pulverized and homogenized.

All 6 of these SRM's were obtained in powdered form in glass bottles, as supplied from their source organizations, thus ready for digestion into solution. As these powders had been sitting for an unknown amount of time, some differential settling of the powdered material had likely occurred, as well as adsorption of moisture onto the particles. As briefly discussed in the Sample Digestion section of Appendix A, an attempt to re-homogenize the contents of the jars was made by this researcher, as well as driving off of any adsorbed moisture by gentle heating of a small portion of each powder prior to sample collection for digestion with subsequent analysis.

Secondary Standards

"Secondary Standard" is the designation used here for each of the 2 USGS In-House Standards included in this project, also listed in Table B-1. The composition of this type of reference material is known to a lesser degree than that of the SRM's, thus is secondary in importance under the initial classification. These standards consist of: 1 geological material (Pikes Peak Granite, from an unnamed location along the Front Range of Colorado, USA), and 1 geochemical material (an agricultural soil from San Joaquin Valley, California, USA). These 2 materials are used exclusively as in-house reference materials within the USGS (Allen Meier, verbal communication 1/12/1999); their inclusion in this project was due to the use of USGS facilities and instrumentation for obtaining the chemical analyses.

These materials were in pulverized form and each housed in a large (1000-ml size) Teflon bottle. However, both were somewhat heterogeneous in composition, as evidenced by visible mineral grains (partially incompletely pulverized material) and stratification of these particles within the bottles, with PPG having a noticeably larger particle size, and larger particle size range, than SJS. The largest SJS particles were in the fine-sized sand range (up to 250 μm; Jackson 1997), while the largest PPG particles lay in the medium-sized sand range (up to 350 μm; Jackson 1997). The larger particle sizes and size ranges, coupled with particle stratification, strongly suggest that heterogeneity may be a problem for these reference materials.

However, according to Allen Meier, USGS (verbal communication 1/12/1999), truly homogeneous samples of these 2 materials are thought not to be necessary, because:

1) all USGS researchers using these reference materials analyze them in this same somewhat heterogeneous condition, thus obtaining and reporting a range of analytical values for them; and, 2) as evidenced by the particle size ranges and stratification, the original soil (SJS) and rock (PPG) specimens had been purposefully processed incompletely. These 2 materials have both been in use as USGS in-house reference materials for at least 5 years (5 years before 1999, so since about 1994), thus the ranges for the for their compositions are fairly well-known (Allen Meier, verbal communication 1/12/1999). However, the only data regarding the "accepted values" for the compositions of SJS and PPG that this author was able to obtain did not provide the compositions of these materials as ranges, but as single data points for each element. This lone source of compositional data consisted of an undated in-house USGS circular, entitled "Accepted Values for In-House Standards" (USGS undated) a copy of which had been obtained directly from a USGS researcher, Dr. James Crock, on 4/27/1999.

Just as with the 6 Primary Standards, the bottles of the 2 Secondary Standards had been sitting for an unknown amount of time and may have adsorbed some moisture; similar procedures were performed on these materials, from attempts to re-homogenize the contents to gentle heating of small portions of each (larger portions, ~2g, than that for the SRM's). This researcher did not expend effort beyond this attempting to obtain more homogeneous samples of these materials. Aside from re-pulverizing the entire contents of each of these bottles (if not the entire batches from which these bottles came), there was no way to significantly improve the homogeneity of these materials beyond this. Therefore, these standards yielded analytical results that show a wider, less well-constrained compositional range than many of the more homogeneously-powdered SRM's. This is discussed in the Analytical Precision and Accuracy section of this Appendix, and can be seen in Tables B-3 through B-30 at the end of this Appendix.

Other Reference Materials

The term "Other Reference Material" (ORM) designates samples of 3 obsidian flows analyzed in this project, whose compositions were partially-known or unknown (see Table B-1). Samples from 2 of these flows, Pachuca, State of Hidalgo, Mexico (referred to here as "PHM"), and Little Glass Buttes, Oregon, USA ("LGB"), were very kindly provided for this project by Dr. Michael D. Glascock, Senior Research Scientist and Leader, Archaeometry Laboratory, Missouri University Research Reactor (MURR), University of Missouri, Columbia, Missouri, USA. He has been developing these 2 materials as inter-laboratory standards and provides samples to other researchers in exchange for their data for these materials (Michael Glascock, written communication 4/22/1997), and has published some of these data (Glascock 1999). The piece (~4.5 g) of PHM obsidian used here had been chipped from the large chunk (~40 lb.) collected from the Pachuca obsidian flow in 1980-1981; similarly, the piece (~5.4 g) of LGB obsidian used here had been chipped from the large chunk (~10 kg) collected from the Little Glass Buttes obsidian flow in 1996 (Michael Glascock, written communication 4/22/1997). The third ORM is comprised of 3 moderately-large chunks of obsidian (>20 g each) from a flow within the Long Valley Caldera complex, California, USA ("LVC"), kindly provided by Dr. Ronald Klusman, Department of Chemistry and Geochemistry, CSM, in 1999. Although there are some published compositional data for Pachuca, Little Glass Buttes, and Long Valley obsidians, it is not known if the collection locations for those previous samples coincide with the collection locations for the samples studied here. Therefore, only the single previous data set for PHM and LGB (Glascock 1999) is used here, as these data are from samples broken from the same large chunk of each as the samples used here, and the composition of LVC was considered unknown. LVC was included in this study as an ORM as compositional information for this material are to be gathered in anticipation of its later use as an in-house standard at CSM (E. Craig Simmons, verbal communication January 1999).

All 3 of the ORM's were obtained in solid form, thus necessitating the cleaning, crushing, and pulverizing steps described in Appendix A to prepare them for digestion into solution. Although it is likely that all 3 original pieces of LVC had been collected at or very near the same place along the flow, this is not known for certain (E. Craig Simmons, verbal communication January 1999); correspondingly, the amount of heterogeneity within the flow as represented by these 3 pieces is also not known. The ideal powdered sample of this material could be obtained by pulverizing all 3 of these pieces, combining all the powder and mixing it until homogeneous. However, that level of homogeneity is not strictly necessary, as this material is intended for use as an intralaboratory standard ("in-house," for use only within CSM) only (E. Craig Simmons, verbal communication January 1999). In addition, all 3 of the pieces contained a number of weathered and/or chemically altered portions. As briefly discussed in Appendix A, Sample Crushing section, the 3 pieces were first broken into fragments (after 3 thin sections were prepared from the largest piece), numerous small pieces containing no alteration or weathering were selected from among these fragments (~3 g total each from each of the 3 original pieces), and these were combined to make the ~10.5 g sample designated as LVC, as used in this study. One thin section was also prepared from each of the single pieces of PHM and LGB, prior to their being crushed and pulverized.

As briefly discussed in Appendix A, Optical Studies section, the solid pieces of all 3 ORM's were observed in an initial optical study via plane polarized light binocular microscope (at up to 40x magnification) housed in the Chemistry and Geochemistry Department, CSM, and a 10x magnification hand lens, owned by the author of this study, for recording of their physical (external and internal) characteristics; the results are given below. The pieces of PHM and LGB were mostly translucent, and some portions transparent. The 3 original chunks of LVC were mostly opaque due to their thickness, although the broken pieces were thinner, less opaque, thus easier to observe. The pieces of the 3 ORM's had both worked and unworked surfaces. Their worked surfaces were very fresh and vitreous; this follows as the pieces had been broken from their respective obsidian flows quite recently. The pieces of LGB and PHM revealed no phenocrysts or structures that would (should) cause the pulverized powders to be difficult to digest (except 2 items regarding PHM, addressed below). The LVC fragments revealed some shadowy "bands," which later thin section observation (addressed below) revealed to be probably due to either flow structures or welding. The larger LVC piece was also broken into smaller pieces after the thin sections were prepared from it, and observations revealed that these were extremely similar to the other pieces of LVC.

A second optical study consisted of observing and recording the internal characteristics of each ORM sample from at least one thin section prepared from that material. Only 1 thin section each was prepared from the PHM and LGB pieces, as these were both quite small in size and mass, and it was of utmost importance to retain as much of each of these samples as possible for chemical analysis, as the more representative they will then be of the entire piece. As mentioned earlier, all 3 original pieces of LVC contained weathered and/or altered portions. Three thin sections were prepared from the largest piece, and great care was taken to obtain the thin sections (each from a different area of the piece) from fresh, unaltered portions of the obsidian. The thin sections of the 3 ORM's revealed that these materials ranged from extremely homogeneous (LGB), to quite homogeneous (LVC), to possibly quite heterogeneous (PHM). No microlites (also called microphenocrysts, very tiny crystals, usually <1 mm to <<<1 mm in size, and typically found in obsidian) or banding of microlites (close association of microlites into streaks or bands) were observed in any of the thin sections in either type of light, except 2 microlites observed in PHM as addressed below. The thin section of LGB revealed this material to be extremely homogeneous, with no microlites or banding observed.

Swirls of a light brown to tan color were observed (under both types of light) throughout all 3 of the LVC thin sections. This pattern or structure is typically observed in obsidian flows that underwent moderate to extensive folding, or deposits of pyroclastic materials that underwent welding (see: Best 2003; Friedman and Long 1984; Hall 1996; LeMaitre 2002; Ross and Smith 1961; Wilson 1989). As the pieces of LVC obsidian provided in this study are of high-quality obsidian (obsidian that contains few to no microlites, and retains much "usable" obsidian in its' mass; see Chapter 2), it is more likely that this obsidian formed from flows that underwent some amount of folding as it formed rather than welding of pyroclastic materials. However, welding together of pyroclastic materials is not entirely unlikely, if it occurred at a high enough temperature to remove most traces of the welds, leaving high-quality obsidian.

Within the whole, uncut piece of PHM, 2 small (<1 mm) microlitic structures were observed, consisting of numerous "arms" of straight and curved microlites radiating outward from a single center. The accepted term for such structures is "trichites," according to the American Geological Institute (Jackson 1997; Neuendorf et al. 2005), although such structures have been termed "asteroidal trichites" elsewhere (Northwest Research Obsidian Studies Laboratory [NROS] 2006; Skinner 1983:41-44, 143-151, 309-310, 373-375). Within the piece of PHM, one of the trichites was observed to have approximately 12 arms, and the other approximately 20 arms; due to the shape of the piece, it was difficult to determine the exact number of arms, although the given approximations are as close as possible. None of the arms of either of these structures in the piece of PHM were observed to curve back into the center of the structure, although some "asteroidal" trichites have some, or all, that do so (NROS 2006; Skinner 1983:41-44, 143-151, 309-310, 373-375). This study's author had deeply hoped that the thin section prepared from the piece of PHM would capture one of these trichites, and the exact location of each had been marked on the piece. However, due to the nature of preparing thin sections, it is difficult to capture structures of such a tiny size, and unfortunately neither of the observed trichites was captured in the prepared thin section. A more precise description of the form, shape, and size of one of these structures would have been valuable information, as it is not known at this time if these types of structures are common in the PHM obsidian. Any information gained about them may help to more completely describe that obsidian source, and thus more completely characterize it.

A small (~1 mm) point of shattering, or possibly a weathering nucleus, was observed on the surface of the piece of PHM. This spot exhibited both weathering (it appeared to be overall somewhat dullish-looking) and shattering (it appeared to consist of tiny broken shards radiating outward from a single point on an outer edge) characteristics. At greater magnification, all of the tiny shards were observed to have a vitreous luster. Thus it is quite likely that the piece had been knocked against something hard during shipping, and it is a small spot of impact shattering. Therefore, the entire piece was crushed and pulverized, with great confidence that the spot had been correctly identified as an area of shattering. If it had been incorrectly identified, and it was indeed a weathering nucleus, the chemical effects of such alteration would (should) be greatly overshadowed by the chemistry of the bulk of the sample (see Chapter 2).

None of the obsidian flows represented by the 3 ORM's were considered to be sources of material from which the obsidian artifacts included in this project had been fashioned. This is due to the vast distances between the archaeological sites studied here and 2 of the ORM's, and the distinct coloration of the third ORM, which is not seen among the obsidian artifacts studied here. Both LGB and LVC are in the United States, Oregon and California, respectively; the distance between these obsidian flows and the archaeological sites from which the artifacts studied here were unearthed (in and near Managua, Nicaragua) is quite large, ~4510-4830 km (~2800-3000 miles). The PHM obsidian is in the State of Hidalgo, Mexico, and its distance to the archaeological sites is much closer, ~1610 km (~1000 miles), though still a fairly large distance. As discussed more fully in Chapter 3, a prodigious number of studies have addressed the question of the possible maximum length of ancient obsidian trade routes. The longest distances this researcher has encountered in the literature are ~1100 km, or ~685 miles (Moholy-Nagy 2003) to ~1200 km, or ~750 miles (Braswell and Glascock 2002:38), with the most extreme example being ~1800 km, or ~1120 miles (Barker et al. 2002). The strata from which the 100 artifacts studied here were recovered ranged from possibly as old as 2000 BC to possibly as recent as 1520 AD; this range of dates was obtained from study of the ceramic and pottery pieces also recovered from the archaeological sites (Bargnesi et al. 1996; Brown et al. 1996; Finlayson 1996; González Rivas et al. 1996; Keller et al. 1996; Pullen 1995; Stauber 1996). It is unlikely that peoples of that time period could, or would, travel or trade over such vast distances to obtain obsidian, although it is not outside the range of possibility. However, as there are obsidian sources located so much closer than these 3 ORM flows (see Chapter 3), this longer-distance movement or trade seems that much less likely. In addition, the PHM obsidian flow is a very distinct apple or bottle green to a gold-green (Michael Glascock, written communication 4/22/1997), and not one of the 96 obsidian artifacts studied here was of any shade of green (see Appendix C for artifact descriptions).

Analytical Precision and Accuracy

Three different methods were employed in this study to gather information regarding either the accuracy or precision of the analytical measurements obtained here. The first method, which provides information regarding accuracy, involved the measurement of the composition of the same SRM's in all analytical runs performed in this study. These particular materials have been analyzed so thoroughly that their compositions are said to be "well-characterized" or "well-constrained." This means that their compositions are very well-known or well-defined, and indeed, each is issued a Certificate of Analysis (or equivalent) stating its' composition (see Table B-1). The compositional values as measured in this study were compared with their "true" (well-characterized, or "accepted") values. This method allows for a determination of the accuracy (closeness of measured values to accepted values) obtained for the analytical methodology used in this study. See Accuracy section below for the discussion.

The second and third methods were both used to provide information regarding precision. These methods allow for determination of the precision (degree of repeatability of measured values) obtained for the analytical methodology used here. The second method involved the measurement of 2 separate portions (duplicate portions) of certain ORM's and debitage samples within the same analytical run. These "duplicates" are separate portions of the sample powders, and were subjected to the same methodology of digestion through analysis as the first portions of these sample powders, thereby obtaining 2 separate yet "duplicate" analyses of these materials. The ORM compositions are either unknown or known to a small degree of certainty, while the debitage sample compositions are unknown. See Precision section below.

The third method involved obtaining second measurements on single portions of certain digested samples. These "repeat" measurements were performed upon certain single aliquot samples not only as a routine part of the instrumental analysis, but also upon certain other single aliquot samples. The routine "repeats" are performed on the first non-reference material sample of each run, and every 10th non-reference material sample thereafter. These routine "repeats" assist in maintaining the performance of the instrument during the entire duration of each analytical run (Allen Meier, verbal communication 1/12/1999). The additional repeated analyses were performed on the very lowest mass debitage piece samples and all 3 ORM's. The very lowest mass samples were those of such a small mass that the entire sample was used to obtain just one portion for digestion (0.2 g ± 0.002 g). As nothing remained for performing another analysis, it was extremely desirable to gain as much information as possible from their single digestion aliquots. As addressed under the Precision section below, it is extremely unfortunate that not one of the repeated measurements for any of these "one-shot" debitage piece samples were deemed useable.

Analytical Runs

As discussed briefly in Appendix A, Sample Digestion section, 3 digestion runs of 50 analytical samples each had been needed in order to prepare all 100 debitage samples for analysis. Each of these 3 digestion runs included 3 blanks, all 6 Primary Standards, 1 or 2 of the 2 Secondary Standards, all 3 ORM's, and 33 or 34 debitage samples. This configuration left room for the addition of 3 sample "duplicates" per digestion run (see Sample Duplicates section, below, for more details). Therefore, there were "duplicate" analyses obtained for these samples. Run 1 contained all 3 blanks, all 6 Primary Standards, both Secondary Standards, all 3 ORM's, 33 debitage samples, and sample duplicates of debitage pieces CS-08 and CS-18 and ORM LGB. Run 2 followed the very same pattern as Run 1, with the sample duplicates being of debitage pieces VT-01 and VT-16 and ORM PHM. After Runs 1 & 2 were completed, there were 34 debitage pieces remaining to be analyzed. Therefore, leaving the Secondary Standard PPG out of Run 3 made room for the 34th debitage piece and still allowed inclusion of 3 sample duplicates. The sample duplicates in Run 3 were of pieces MO-03 and VT-15 and ORM LVC.

Analytical Data and Tables

The analytical data obtained in this study via ICP-MS for the reference materials, is presented in Tables B-3 through B-30 (placed at the end of this Appendix, for clarity and ease of presentation of the text), with each table containing information for 1 element only. This data set consists of information for 28 elements: Al, Ba, Ca, Ce, Cr, Cs, Cu, Fe, K, Ga, La, Li, Mg, Mn, Na, Nb, Ni, Pb, Rb, Sr, Ta, Th, Tl, U, V, W, Y, and Zn. Note that the new groupings for the reference materials are used: "Critical Standards" for those standards composed of obsidian, the material of primary interest in this present study, and for which there are "certified," or equivalent, compositional data; "Supplementary Standards" for the ORM's PHM, LGB and LVC, also obsidians, but materials for which little or no chemical data exist; and "Additional Standards" for those standards composed of other lithic materials, for which various amounts and qualities of chemical data exist. Table C-1, Appendix C, presents the chemical data for the debitage pieces obtained in this study.

The ICP-MS used to obtain the chemical analyses in this study has the capability of capturing chemical data for 42 elements virtually simultaneously (Allen Meier, verbal communication 1/12/1999), and indeed, the chemical data for the samples studied here included a total of 42 elements (Ag, Al, As, Au, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sb, Sc, Se, Sr, Ta, Te, Th, Tl, U, V, W, Y, and Zn). However, upon inspection of the data, it was observed that the analyses for the standards and reference materials for a total of 14 of these elements were found to be either at or below detection limits, and thus the data for these elements were unusable (Ag, As, Au, Be, Cd, Co, Ge, In, Mo, P, Sb, Sc Se, and Te). Only the analytical data for those 28 elements that were found to be significantly above detection limits is presented (see Tables B-3 through B-30) and discussed in this study.

Tables B-3 through B-30 present the results for the 28 elements (1 element per table) for each of the 3 analytical runs ("Run 1 Value," "Run 2 Value," and "Run 3 Value"), plus the calculated mean ("Mean Value") of these 3 runs. All of these data are given in 3 significant digits. In addition, the calculated mean value is compared to the known published value ("Accepted Value") of each standard, and the calculated difference between the mean and the known value is presented ("Percent Difference"), to 2 decimal places. See both Accuracy and Precision sections, below, for more detailed information. If interested, the reader may see Govindaraju (1984, 1994) or Flanagan (1986) for information regarding how "accepted" values are determined, as explanation and details of this procedure is beyond the scope of this present study.

Sample Duplicates

A sample "duplicate" consists of another, or duplicate, portion taken from a given powdered sample, and is subjected to the same preparation and analytical procedures as the first sample portion, from digestion using the 4-acid procedure through instrumental analysis via ICP-MS. Thus, a sample duplicate of a given powdered sample consists of a second 0.2 g (± 0.002 g) portion of the sample powder, resulting in a second digestion aliquot (digested liquid) of that sample. The results for the analyses obtained in this study for both initial and duplicate portions for all 6 debitage pieces and 3 ORM's that were duplicated is given in Table B-2 (presented under Precision section, later in this Appendix). The particular debitage pieces chosen for duplicate analysis in this manner were those with the highest masses in their respective digestion runs, thus: CS-08 and CS-18 in Run 1; VT-01 and VT-16 in Run 2; and MO-03 and VT-15 in Run 3. Duplicate analyses of each of the 3 ORM's were performed (LGB in Run 1, PHM in Run

2, and LVC in Run 3) to gain more information about these materials, for which little or no previous chemical data existed. Although it is extremely desirable to perform numerous duplicate analyses such as these when performing chemical analyses, the analytical facilities utilized in this study were available in an extremely limited capacity. Strict minimization of the number of digestion and analytical runs was necessitated, thus allowing for only a small number of sample duplicates. Although only a minimum number of duplicates were performed in this study, these provided valuable information.

Analysis of both of the duplicate digested portions of a given sample yields information about the variation in composition of that sample, and therefore the entire piece from which both powdered portions were taken. Homogenization of an entire pulverized sample prior to removal of the two 0.2 g (± 0.002 g) portions leads to each portion having the same composition. Owing to the remarkably homogenous nature of obsidian, the assumption can be made that the homogenized powdered sample very nearly represents the composition of the entire obsidian flow from which that sample had been collected. Thus, the composition of an obsidian debitage sample can be taken to represent the composition of the obsidian flow from which that piece had been fashioned. Although this appears to be a rather broad assumption, it is appropriate if applied in a general way. The validity of applying this assumption to the samples of obsidian debitage pieces and obsidian reference materials (all 3 ORM's, as well as Primary Standards RGM-1 and SRM-278) is appropriate. However, the materials from which the 4 other artifacts had been fashioned (quartz, silicified conglomerate, and pottery), as well as the materials comprising the 6 non-obsidian standards and reference materials (agricultural soil, basalt, granite, and sediment), analyzed here are more heterogeneous in composition than obsidian. Therefore, these materials are not strictly representative of the entire material from which they were taken. Yet, the assumption can still be reasonably made for the purposes of this study, as these materials are outside its scope. See Precision section later in this Appendix for further discussion.

Repeat Measurements

Repeated measurements were also performed here during the analysis of all 3 analytical runs. These "repeats" consisted of a second ICP-MS measurement of the composition of a given digested sample portion, and were performed within the same analytical run, and on the same aliquot as the first measurement. Thus, both the first and repeat analyses were performed on a single digestion aliquot obtained from one 0.2 g (± 0.002 g) portion of a given powdered sample. As mentioned earlier, repeat analyses are routinely performed on certain single sample aliquots as part of the instrumental protocol in order to maintain instrument performance during the duration of the analytical run (Allen Meier, verbal communication 1/12/1999); these repeats were performed during each of the 3 analytical runs here on all 3 blanks, all 6 Primary Standards, and both Secondary Standards. A number of repeat analyses on other single digestion aliquots were also performed; these additional repeats were performed on the very lowest mass debitage samples, as well as all 3 ORM's and 4 other debitage samples within each run.

The very lowest mass debitage samples were those of such a small mass (≤0.200 g) that the entire sample was used up in order to obtain just one digestion portion of 0.2 g (± 0.002 g). It was extremely desirable to gain as much information as possible from these "one-shot" samples, as there was no possibility for another analysis. There were 8 such lowest mass debitage samples: CS-07 and CS-11 in Run 1; and CS-01, VT-35, VT-36, VT-37, VT-38 and VT-42 in Run 3. The analytical methodology used with the ICP-MS routinely takes repeat measurements of the first non-reference material sample of the run and then every 10th non-reference material sample thereafter run (Allen Meier, verbal communication 1/12/1999). These automatically-performed repeats thus comprise the 4 other debitage samples that had been subjected to repeat analysis in each run: CS-02, CS-15, CS-25 and LP-01 in Run 1; CS-06, MO-02, VT-10 and VT-23 in Run 2; and CS-01, VT-02, VT-31 and VT-41 in Run 3. See Precision section, below, for more information.

Accuracy

As stated earlier, accuracy refers to how close the measurements of a given material are to its "true," or accepted, value. Therefore, good accuracy within a population of measured values for a given sample will be revealed as a close correlation between those measured values and the accepted value for that material. In order to determine how accurate a set of measured values is for a given material, the accepted value of that material must be known. Because the artifacts in this study have unknown compositions, their analyses could not yield information regarding accuracy; likewise with the ORM LVC, whose composition is also unknown. The compositions of the ORM's LGB and PHM are known to only a small degree of certainty, and thus these materials could yield only limited information regarding accuracy. As the known values of the 2 Secondary Standards (PPG and SJS) are not well-constrained (see Secondary Standards section of this Appendix), and thus not well-known, they, too, could yield only limited information regarding accuracy as well.

The compositions of the remaining reference materials used in this study, namely the Primary Standards SRM-278, RGM-1, BCR-1, BHVO-1, SRM-2709 and GSD-5, are well-known, or well-constrained, thus their "true," or accepted, compositions are known. The compositions of these reference materials have been so thoroughly analyzed that the composition of each is stated on a Certificate of Analysis (see Table B-1), or equivalent. The accuracy of the measured compositional values for the 6 Primary Standards as obtained in this study can be determined when those values are compared with the true (certified) values for those materials. Tables B-3 through B-30 (presented at the end of this Appendix) contain this data in tabular format, with each table containing the information for only 1 element. As addressed earlier in this Appendix, a total of 42 elements were analyzed in this study; however, for 14 of these elements, the analytical data were either at or below detection limits, thus this data was unusable. Therefore, the analytical data for a total of 28 elements is presented and discussed here (and in Tables B-3 through B-30): Al, Ba, Ca, Ce, Cr, Cs, Cu, Fe, K, Ga, La, Li, Mg, Mn, Na, Nb, Ni, Pb, Rb, Sr, Ta, Th, Tl, U, V, W, Y, and Zn. In addition to the measured and accepted (certified) values for all 6 Primary Standards, these tables also contain the measured values and accepted values for both Secondary Standards and 2 of the 3 ORM's; ORM LVC lacks a previously-known value, thus the measured values only are given.

Note that Tables B-3 through B-30 list the reference materials used in this study in a different manner than that shown in Table B-1. As stated briefly early in this Appendix, and below in more detail, the reference materials have been reorganized into a different set of categories based mainly upon their overall composition, and secondly on how well-constrained their compositional information. These new categories separate the most useful of the reference materials for determining the accuracy of the measured values from those of lesser importance in this respect. The order of importance for the reference materials in determining the accuracy is roughly equivalent to how they are listed in Tables B-3 through B-30.

Because the artifacts of interest here are composed of obsidian, the reference materials composed of obsidian were of critical importance for determining the accuracy of the measured values; these are SRM-278 and RGM-1, both formerly classified as Primary Standards, and PHM, LGB and LVC, all formerly classified as Other Reference Materials. Both SRM-278 and RGM-1 have well-characterized compositions, and are now considered to be "Critical Standards" as they are critical for determining the accuracy of the measured values obtained here. However, as the compositions of PHM, LGB, and LVC are either unknown or much less well-known, they are of limited use in determining accuracy, and are now re-classified hereafter as "Supplemental Standards."

The remaining reference materials are composed of other geological/geochemical materials, which differ in varying degrees from obsidian, and are hereafter classified as "Additional Standards." These include a granite (PPG, formerly a Secondary Standard), 2 basalts (BCR-1 and BHVO-1, both formerly Primary Standards), 2 agricultural soils (SRM-2709, formerly a Primary Standard, and SJS, formerly a Secondary Standard), and a sediment (GSD-5, formerly a Primary Standard). Although PPG is a granite, whose composition is closer to obsidian than all the other remaining standards, its' composition is not well-constrained (discussed under the Secondary Standards section in this Appendix). Thus, its use for determining accuracy is more limited than that of the obsidians (Critical Standards SRM-1 and RGM-1). The rest of the standards (basalts, agricultural soil, and sediment) are quite different in composition from that of obsidian. Although 4 of these 5 have well-constrained compositions (BCR-1, BHVO-1, SRM-2709 and GSD-5), they too, have somewhat limited usefulness in obtaining accuracy information because of the much wider difference in composition from obsidian.

Below, the results for the standards are discussed under their new categories, and what these results mean regarding accuracy. As an example, Table B-4 contains all pertinent data for all of the reference materials as obtained in this study for the element barium (Ba). The value for each reference material as obtained from Certificates of

Analysis or other similar published sources has been listed as its "Accepted Value," and the sources of this data noted in the table. The values for the reference materials as measured in the first analytical run performed in this study are listed as "Run 1 Values;" similarly, the values measured in the second analytical run are listed as "Run 2 Values," and those for the third analytical run are "Run 3 Values." The "Mean Values" listed are the arithmetic means (averages), of the 3 measured ("Run") values; although any listed values below detection limit (such as "<0.1 ppm" for Cs) were not included in determinations of the Mean Values. All 4 of these values are presented in 3 significant digits. As discussed in the Precision section in this Appendix, the 3 Supplemental Standards (PHM, LGB and LVC) were subjected to "duplication," one in each of the 3 analytical runs. This means that in each of the 3 runs, 2 separate portions of one Supplemental Standard had been digested and analyzed. Thus, the "Run 1 Values" for LGB are actually the arithmetic means of the values for the 2 separately-analyzed aliquots; likewise for the "Run 2 Values" for PHM, and the "Run 3 Values" for LVC. The "Percent Difference" for a given reference material is calculated using the following equation, and presented to 2 decimal places:

$$\text{Percent Difference} = \frac{(\text{Mean Value} - \text{Accepted Value})}{(\text{Accepted Value})} \times 100$$

The Percent Difference relates how much the analytical values (as Mean Values) vary from the Accepted Values, thus giving a measure of the accuracy achieved in this study. Although the exact measure of accuracy is dependent on many factors, in general, the smaller the calculated Percent Difference, the greater the accuracy achieved. Continuing with the example begun above, the mean of the analytical values for the Critical Standard SRM-278 varies for Ba from the Accepted (Certified) Value by +0.23%, and that for the other Critical Standard RGM-1 varies by –0.12%. This means that the analytically determined values for Ba for SRM-278 (Runs 1 through 3 Values) were 0.23% higher, on average, than the Accepted Value for that standard, while those for Ba for SRM-278 were 0.12% lower on average than the Accepted Value. It is of great importance in this study that the Critical Standards, those composed of obsidian and having Certified (well-constrained) Values, achieve the lowest calculated Percent Differences, as obsidian is the material of greatest interest here. It is of importance that the other standards also achieve low Percent Differences; however, as these standards are composed of materials quite different from obsidian, it is not quite as critical.

Critical Standards. As shown in Tables B-3 through B-30 (at the end of this Appendix), nearly all (25) of the 28 elements studied here yielded Percent Differences within ± ~5% of the Accepted Values for the 2 Critical Standards, SRM-278 and RGM-1 (Al, Ba, Ca, Ce, Cr, Cs, Fe, K, La, Li, Mg, Mn, Na, Nb, Pb, Rb, Sr, Ta, Th, Tl, U, V, W, Y, Zn). These 2 standards were both initially classified in this study as Primary Standards, as seen in Table B-1, and addressed earlier. Only 3 elements have Percent Differences significantly outside this range: Cu (+15.76% and -23.92%, respectively), Ga (+26.92% and -0.67%), and Ni (-0.56% and -52.95%). Percent Differences for nearly half (12) of the 28 elements were ± 3% (Ba, Ca, Ce, Fe, K, Li, Na, Pb, Rb, Sr, Th and W), and most of those (10) were within ± 2% (Ba, Ca, Fe, K, Li, Na, Pb, Rb, Th and W). Another 6 elements were between ± 3% and ± 5% (La, Mg, Nb, Ta, Tl and Y). There was no published data available for either Li or W for SRM-278.

It is unclear as to why the Cu values obtained here for the Critical Standards varied so widely from the Accepted Values. However, both Critical Standards (SRM-278 and RGM-1) and 2 Additional Standards (BCR-1 and PPG), all of which have the lowest Accepted Values (5.9, 12, 11, and 19 ppm, respectively), also attained the greatest Percent Differences for this element (+15.76%, -23.92%, -20.55%, and -25.79%). The Accepted Values of these standards are quite a bit lower than the next higher standards (34.6 and 40 ppm), and significantly lower than the remaining standards (136 and 137 ppm). Although Briggs and Meyer (1999) made no mention of lower Cu values being problematic to measure by ICP-MS, perhaps the actual running conditions served to make this so. The Ni values are an almost complete replication of this "pattern," in that the standards with the lowest Accepted Values attained the greatest degree of Percent Difference, except in the lone case of Critical Standard SRM-278. The implication of this possible pattern regarding the analytical results obtained for the 100 debitage pieces studied here is that the lower Cu and Ni values may have a greater degree of uncertainty, thus a higher degree of variation, associated with them. Only one Ga value is significantly outside ± ~5%, that for SRM-278 (+26.92%); there seems to be no correlation between this higher Percent Difference and the lower Accepted Value range, or any other plausible reason this researcher can offer for explanation.

Supplemental Standards. Also shown in Tables B-3 through B-30 (at the end of this Appendix) are the analytical values obtained here for the 3 Supplemental Standards (all initially classified as Other Reference Materials), PHM, LGB and LVC. As stated earlier, all 3 Supplemental Standards have compositions that are either unknown (LVC) or known to a small degree of certainty (one published analysis each for PHM and LGB). The calculated Percent Differences for PHM and LGB are presented in these tables also, and are revealed to have quite a wide range for these materials. This calculated difference ranged from as close to the single published values as +0.79% (PHM) and +1.76% (LGB) for Na, to as far from the single published values as +29.32% (PHM) and +34.52% (LGB) for Zn, +18.35% (PHM) and +45.16% (LGB) for Fe, and -54.33% (PHM) for Ba. The only other elements with Percent Differences significantly over ± ~5% were La (+10.36% for PHM, +13.18% for LGB), Th (+18.44% for PHM, +14.39% for LGB), and U (+10.72% for PHM). However, none of these are necessarily unreasonable for materials about which so little information is available.

There was published compositional data available for both PHM and LGB for not quite half (13) of the 28 elements studied here, including Ba, Ce, Cs, Fe, K, La, Mn, Na, Rb, Ta, Th, U and Zn. There was also published compositional data for Sr for LGB, but not for PHM. There was no published compositional data available for either PHM or LGB for the nearly half (14) of the elements studied here (Al, Ca, Cr, Cu, Ga, Li, Mg, Nb, Ni, Pb, Tl, V, W and Y). There was no previous chemical data available for LVC with which to compare any of the values obtained here, as noted earlier.

These 3 materials were included in this study in order to obtain either more (in the case of PHM and LGB), or initial (in the case of LVC), chemical data about them. The variation seen in the data for these materials, and as revealed by the differences between the 3 Run Values, and the Percent Differences for PHM and LGB (see Tables B-3 through B-30), can provide an approximation of the natural variation in the composition of these materials. However, several data for PHM and LGB show significant Percent Differences, the magnitude of which may not be due to natural compositional variations.

For Ba, PHM yielded a Percent Difference of –54.33%, which was by far the greatest Percent Difference for any standard for this element. There was one other previously-published value for Ba for PHM, that of 19 ppm, obtained by Glascock et al. (1988), but was not used here, as the Accepted Value was superseded by Glascock's (1999) value of 30 ppm. However, both of these values have rather high reported "deviations" (± 12 ppm in each case, thus ± ~63% for the 1988 value and ± ~40% for the 1999 value), therefore both values have a high degree of uncertainty. In addition, the PHM Ba analytical values are by far the lowest (Mean Value of 13.7 ppm) of any standard (Mean Values ranging from 122 through 1340 ppm). The implication of this may be that those debitage pieces with Ba values in this lower range may have a higher degree of uncertainty associated with their analytical values.

Although there appears to be a fairly large Percent Difference between the Mean Value and Accepted Value for Fe for PHM (+18.35%), this may not be overly large. As stated earlier, this large a difference may be due to natural compositional differences. As the only other large Fe Percent Differences for any standard were for LGB (+45.16%), this may be likely. Also, this large Percent Difference for Fe for LGB may be due to that Mean Value being the lowest (9000 ppm) of all the standards. The implication for this would be similar to that indicated above for Ba, in that those debitage pieces with lower Fe values may have a larger degree of uncertainty associated with those values.

Both PHM and LGB appear to have fairly large Percent Differences between their Mean Values and their Accepted Values for Th (+18.44% and +14.39%, respectively), although these, too, may not be overly large. Thorium (Th) is a notoriously difficult element to keep in solution (E. Craig Simmons, verbal communication January 1999), and it often precipitates out of a prepared solution if the solution has experienced a waiting period of any length between digestion and analysis. Although all 3 analytical runs in this study did experience wait times between digestion and analysis (Allen Meier, verbal communication 4/22/1999), the exact length of these periods are unknown to this researcher. As noted earlier in this Appendix, the analytical facilities, was extremely limited, and the analyst very kindly fit the 3 analytical runs of this study in-between his many other analytical runs and other duties. However, the author of this study does not believe that Th had come out of these prepared digestion solutions to any significant degree; if this was the case, the Th values would have been low, rather than high as is seen here. As the only other standard (the Additional Standard BHVO-1) with a large Percent Difference (+23.64%), has the smallest Accepted Value (1.1 ppm), it is likely that the larger differences seen in Th for PHM and LGB here are due to natural variations in these materials whose compositions are relatively unknown.

Both PHM and LGB appear to have fairly large calculated Percent Differences for Zn (+29.32% and +34.52%, respectively), also. Glascock's (1999) value for PHM of 191 ppm has a reported "deviation" of ± 12 ppm, or ± ~6%, while Glascock et al. (1988) have a value for PHM of 193 ppm (again, the 1988 data was not used in this study) with a "deviation" of ± 24 ppm, or ± ~12%. Similarly, Glascock's (1999) value for LGB of 31 ppm has a reported "deviation" of ± 7 ppm, or ± ~23%. The only other standards with larger Percent Differences for Zn are the Additional Standards SJS (+14.55%) and PPG (+10.91%). These 2 materials are more heterogeneous than any of the other standard materials, addressed directly below, and so more variation would be expected. Thus, it may be quite likely that the larger differences seen for Zn for both PHM and LGB are due to natural compositional variations.

Additional Standards. Presented in Tables B-3 through B-30 (at the end of this Appendix) are the analytical values obtained in this study for the 6 Additional Standards PPG, BCR-1, BHVO-1, SRM-2709, GSD-5 and SJS. As addressed earlier in this Appendix, BCR-1, BHVO-1, SRM-2709 and GSD-5 were all initially classified as Primary Standards, and both PPG and SJS as Secondary Standards. Four of these 6 Additional Standards (BCR-1, BHVO-1, SRM-2709 and GSD-5) have compositions that are well-constrained, and will be discussed directly below. These 4 Additional Standards with well-defined compositions are composed of 3 different lithic materials (basalt, agricultural soil, and sediment). The remaining 2 Additional Standards (PPG, a granite, and SJS, an agricultural soil) have much less well-constrained compositions, and will be discussed farther along.

Although both Additional Standards BCR-1 and BHVO-1 are basalts, their elemental compositions are quite different. The results obtained here for the Additional Standard BCR-1 (a basalt) reveal that just over half (16) of the 28 elements studied here yielded Percent Differences within ± ~5% of the known values (Ba, Ca, Ce, Cs, Fe, Ga, K, Li, Mn, Na, Pb, Rb, Ta, W, Y and Zn). The remaining elements (12) have Percent Differences significantly outside this range: Al (+9.02%), Cr (-16.88%), Cu (-25.79%), La (+12.45%), Mg (+18.57%), Nb (-12.14%), Ni (-25.92%), Sr (+13.03%), Th (+10.70%), Tl (+19.33%), U (+17.14%), and V (+11.06%). Percent Differences for nearly half (9) of the 28 elements were ± 3% (Ba, Cs, K, Li, Mn, Na, Ta, Y and Zn), and two-thirds (6) of those were within ± 2% (K, Li, Mn, Ta, Y, and Zn), while 4 elements were between ± 3% and ± 5% (Ca, Fe, Pb, and Rb).

The BCR-1 "Accepted Value" for Cr used here is a "Proposed Value," not a certified value, thus there is still uncertainty surrounding it, and the calculated Percent Difference of -16.88% may not be unreasonable. The Cu "Accepted Value" is also not a certified value, but a "Proposed Value," and the calculated Percent Difference of -25.79% also may not be unreasonable for this element. The calculated Percent Difference for Mg (+18.57%) appears somewhat high, however the value of Mg for BCR-1 is on the high end, and all standards with Mg values on the high end have calculated Percent Differences that are somewhat higher also. The U value appeared to follow a similar "pattern" but with a twist; the calculated Percent Difference was +17.14%, which appears a bit high, yet the Accepted Value was 1.75 ppm, which is on the low end of the standards here, and all the standards with lower U values also had higher Percent Differences. The Ni values appeared to follow a "pattern" opposite to these 2 elements; the calculated Percent Difference for Ni (-25.92%) is somewhat low, and the value of BCR-1 for Ni is on the low end of the values for the standards, and all the standards with Ni values on the low end also have Percent Differences that are lower. Thallium is somewhat different; the calculated Percent Difference of Tl (+19.33%) appears somewhat high, however the Mean Value obtained here (0.358 ppm) and the Accepted Value (0.3 ppm) are both low, especially compared to the detection limit (0.1 ppm, see Table A-2, Appendix A). The low concentration of the element may have been hard to detect, leading to a greater degree of uncertainty for low concentration analyses.

The results obtained here for the Additional Standard BHVO-1 (a different basalt) show that almost two-thirds (17) of the 28 elements studied here yielded Percent Differences within ± ~5% of the Accepted Values (Al, Ca, Ce, Cu, Fe, K, La, Li, Mn, Na, Nb, Ni, Ta, V, W, Y, and Zn). There was no published compositional data for Tl for BHVO-1. About one-third (9) of the 28 elements have Percent Differences significantly outside this range: Ba (-12.23%), Cr (+15.22%), Cs (-25.38%), Mg (+15.14%), Pb (-16.92%), Rb (-10.91%), Sr (+9.43%), Th (+23.64%), and U (+19.76). Percent Differences for one-quarter (7) of the 28 elements were ± 3% (Cu, Fe, Mn, Na, Ni, V, and Y), and most (5) of those were within ± 2% (Cu, Fe, Na, V, and Y), while 5 elements were between ± 3% and ± 5% (Ce, Ga, K, Nb, and Ta).

The calculated Percent Difference for the BHVO-1 Cr value appears high (+15.22%), but the Accepted Value is a "Recommended Value," not a certified value, and thus a fair degree of uncertainty surrounds this value. Therefore the seemingly high Percent Difference may not be unreasonable. Although the calculated Percent Difference for Mg (+15.14%) appears somewhat high, the value of Mg for BHVO-1 is the highest of all the standards here, and all the standards with Mg values on the high end have calculated Percent Differences that are somewhat higher also. This "pattern" also appears to occur with the U Percent Differences and values. A twist of this "pattern" seems to have occurred with Rb, as it is the lowest of the standards used here, and the lowest value standards also appear to have the higher Percent Differences.

A different "pattern" seems to the case for several other elements for BHVO-1. The calculated Cs Percent Difference (-25.38%) appears to be quite low, however, the Accepted Value for Cs is just 0.13 ppm, which is the lowest value for any of the standards here, and just above the detection limit of 0.1 ppm (see Table A-2, Appendix A). This low concentration can be hard to detect, and there is higher uncertainty associated with such low values. This appeared to be the situation with Pb also, as the value for BHVO-1 is the lowest of all the standards here (2.6 ppm), by nearly an order of magnitude (the next highest is BCR-1 at 13.6 ppm), and is only just over twice the value of the instrument's detection limit (1.0 ppm). This appears to be situation with Th also, in that the BHVO-1 value is once again the lowest (1.1 ppm), with the next highest value half an order of magnitude higher (BCR-1 at 5.98 ppm), and a detection limit of 1.0 ppm.

The results obtained here for the Additional Standard SRM-2709 (agricultural soil) show that nearly all (23) of the 28 elements studied here yielded Percent Differences within ± ~5% of the known values (Al, Ba, Ca, Ce, Cr, Cs, Cu, Fe, Ga, K, La, Mn, Na, Ni, Pb, Rb, Sr, Th, U, V, W, Y, and Zn). There was no published compositional data for Li, Nb or Ta for SRM-2709. Less than one-tenth (2) of the 28 elements have Percent Differences significantly outside this range: Mg (+18.54%) and Tl (–15.81%). Percent Differences for almost half (12) of the elements were ± 3% (Ca, Cr, Cu, K, La, Mn, Na, Pb, Rb, V, W, and Zn), and most (11) of those were within ± 2% (Ca, Cr, Cu, K, La, Na, Pb, Rb, V, W, and Zn), while 1 element was between ± 3% and ± 5% (Fe).

The calculated Percent Difference for SRM-2709 for Mg, +18.54%, appears somewhat high. However, the value of Mg for SRM-2709 is on the high end of the standards here, and all the standards with Mg values on the high end have calculated Percent Differences that are somewhat higher also. The calculated Percent Difference of Tl (-15.81%) appears somewhat low; however, the Accepted Value (0.74 ppm) is somewhat low, and just like with BCR-1, the low concentration of the element as compared to the detection limit (1.0 ppm) probably meant that it was hard to detect at such low concentrations, and thus there is increased uncertainty for such low values.

The results obtained here for the Additional Standard GSD-5 (sediment) show that nearly all (23) of the 28 elements studied here yielded Percent Differences within ± ~5% of the known values (Al, Ba, Ca, Ce, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, Th, Tl, U, V, W, and Zn). Less than one-quarter (5) of the 28 elements have Percent Differences outside this range: Cr (+12.00%), La (-13.70%), Nb (-14.74%), Ta (-11.43%), and Y (-25.38%). Percent Differences for over one-quarter (9) of the elements were ± 3% (Ca, Ce, Fe, K, Li, Mn, Pb, Tl, and V), and most (8) of those were within ± 2% (Ca, Ce, K, Li, Mn, Pb, Tl, and V). The remaining 4 elements were between ± 3% and ± 5% (Cs, Rb, Th, and W).

Although the calculated Percent Difference for GSD-5 for Ta appears a bit low (-11.43%), the Accepted Value for GSD-5 for Ta is a "Recommended Value," not a certified value, and thus has a fair degree of uncertainty surrounding it. In scrutinizing the data, the author of this study is uncertain what the reason(s) may be for the other largish Percent Differences seen for GSD-5 (Cr, La, Nb, and Y), as all these Accepted

Values are "Certified Values." However, the document reporting these values is somewhat dated (Xie et al. 1985), and very little information about these values is known, such as the length of time over which these data have been collected, how many and what types of instruments have been used to obtain these data, detection limits for these instruments, method(s) for compiling these data, etc. Thus, these data are taken at "face value," and used here as such, although again, very little is known about them.

As discussed earlier in this Appendix, Secondary Standards section, two of the Additional Standards (PPG and SJS, formerly classified as Secondary Standards) are more heterogeneous in composition than the other, well-pulverized reference materials. This greater heterogeneity in turn lead to a wider variation in the analyzed compositions for these materials, as evidenced by the greater calculated Percent Differences for both here. As also addressed in the Secondary Standards section, true homogenization of these 2 materials may not have been considered necessary, as gaining more information regarding the possible compositional variation in these materials may have been more desirous than certifying their values (Allen Meier, verbal communication 1/12/1999).

The calculated Percent Differences for PPG and SJS ranged from as close to their single set of "Accepted Values" as +0.33% (PPG) and -1.74% (SJS) for Li, to as far from these "Accepted Values" as +17.71% (PPG) for V, +19.33% (SJS) for Mg, -20.55% (PPG) for Cu, +21.07% (PPG) for Pb, -23.50% (PPG) for Ni, and +94.69% (PPG) and +52.86% (SJS) for Nb. Aside from these, the only other elements with Percent Differences significantly over ± ~5% were Na (+10.00% for PPG), Ce (+10.22% for SJS), Al (+14.86% for PPG), and Zn (+10.91% for PPG, +14.55% for SJS). However, these large differences are not unreasonable for materials that are known to be heterogeneous. There were published compositional data (a single set of values) for both PPG and SJS for nearly all (25) of the 28 elements studied here (Al, Ba, Ca, Ce, Cr, Cu, Fe, Ga, K, La, Li, Mg, Mn, Na, Nb, Ni, Pb, Rb, Sr, Ta, Th, U, V, Y, and Zn). However, the "Accepted Values" for both Ta and U are not number values but more like maximum acceptable values ("<40 ppm" for both PPG and SJS for Ta, and "<100 ppm" for both PPG and SJS for U; USGS undated in-house circular entitled "Accepted Values for In-House Standards"). There was no published compositional data for either PPG or SJS for 3 elements (Cs, Tl, and W).

As may be observed, PPG exhibits larger Percent Differences overall than SJS; this holds very well with the noted greater heterogeneous appearance of PPG versus SJS, as detailed earlier in this Appendix, Secondary Standards section, and briefly here. Both SJS and PPG had noticeably larger particle sizes than the other standards used here, with PPG particle sizes ranging larger than that of SJS, and PPG particles were also be seen to be stratified. In addition to the compositional heterogeneity of these 2 materials, their Accepted Values were reported as single data points rather than as ranges of values, and knowledge of how these values were calculated, as well as the number of analyses, the number and types of analytical instruments used to obtain the analytical information, etc., is also not known to the author of this study. Therefore, it is prudent to suspect that there is more uncertainty associated not only with the "Accepted Values" supplied for these materials, but also with the values obtained for them here as compared to the other standards used. Thus, greater variations in Percent Differences for these 2 materials are likely not as significant as for standards having truly certified values.

Precision

As discussed earlier in this Appendix, 2 methods were used here to provide information regarding the precision (repeatability of measured values) obtained for the analytical methodology used. A good degree of precision achieved in an analytical study means that the measured values are the same value, or very nearly so. Good precision within the population of values for a given sample is an indication that the sample was homogeneous when a portion, or portions, was removed for analysis. However, small differences in measurements for a given sample can occur due to natural variations within the material comprising that sample. Good precision is also an indication that each value was obtained in the same manner, thus instrument sensitivity, operating parameters, and other factors that affect instrumental measurements did not vary to a great degree.

The first of the 2 methods involved using sample "duplicates." A sample "duplicate" consists of a second, or duplicate, portion taken from a given powdered sample, with this second portion of sample being subjected to the same digestion, preparation and analytical procedures as the first sample portion. Thus, after having undergone the digestion procedure, there are 2 aliquots (liquid portions) for the same sample, each having been obtained from a separate powdered portion of that same sample. As discussed earlier in this Appendix, a total of 6 obsidian debitage samples (CS-08 and CS-18 in Run 1, VT-01 and VT-16 in Run 2, and MO-03 and VT-15 in Run 3) and all 3 Supplemental Standards (LGB in Run 1, PHM in Run 2, and LVC in Run 3) were subjected to this procedure. See Sample Duplicates section below for more details, and information regarding how these determinations affect the precision.

The second of the 2 methods involved using sample "repeats." A sample "repeat" consists of a second instrumental analysis performed on the very same aliquot as the first instrumental analysis. Thus, 2 analyses were performed on the single aliquot obtained from the single digested powdered portion of a given sample. As discussed earlier in this Appendix, repeat analyses are routinely performed on certain sample aliquots as part of the instrumental protocol to maintain instrument performance during the duration of a given analytical run (Allen Meier, verbal communication 1/12/1999). These routine repeat analyses were automatically performed during each of the 3 analytical runs in this study on all 3 blanks, all 6 of the standards that had been previously-categorized as Primary Standards (SRM-278, RGM-1, BCR-1, BHVO-1, SRM-2709, and GSD-5), and both standards that were previously-categorized as Secondary Standards (PPG and SJS). The analytical methodology used with the ICP-MS used here automatically performs repeat measurements of the first non-reference sample of the run and then every 10th such sample thereafter. A number of repeat analyses on other samples were also performed in this study, including the very lowest mass obsidian debitage samples (CS-07 and CS-11 in Run 1; and CS-01, VT-35, VT-36, VT-37, VT-38 and VT-42 in Run 3), plus 4 other obsidian debitage samples (CS-02, CS-15, CS-25 and LP-01 in Run 1; CS-06, MO-02, VT-10 and VT-23 in Run 2; and CS-01, VT-02, VT-31 and VT-41 in Run 3), and all 3 Supplemental Standards in each run. The very lowest mass obsidian debitage samples were of such a small mass that the entire sample was used up in obtaining a single portion for digestion and preparation for analysis. These lowest mass obsidian debitage samples were targeted for repeat analysis, as there was one opportunity only in which to obtain compositional information. The automatically-performed repeat samples comprise the 4 other obsidian debitage samples that had been subjected to repeat analysis in each run.

See Sample Repeats section below for more details, and information regarding how these determinations affect the precision.

Sample Duplicates. As discussed above, a sample "duplicate" consists of another, or duplicate, portion taken from a given powdered sample, and subjected to the same digestion, preparation, and analytical procedures as the first portion of that sample. This procedure results in 2 "duplicate" aliquots obtained from the same sample. The obsidian debitage pieces selected for this duplicate analysis were those with the highest masses in their respective digestion runs (CS-08 and CS-18 in Run 1; VT-01 and VT-16 in Run 2; and MO-03 and VT-15 in Run 3). Duplicate analyses of the 3 Supplemental Standards (PHM, LGB and LVC; formerly categorized as Secondary Standards) were performed (LGB in Run 1, PHM in Run 2, and LVC in Run 3) to obtain more information about these materials, for which little or no compositional data existed.

As obsidian is often remarkably homogeneous in composition, the assumption can be made that a (homogeneously-)powdered sample of obsidian represents the whole piece from which it was taken, and thus the entire obsidian flow from which that piece had been taken. This assumption can be validly applied to samples of obsidian debitage pieces and obsidian reference materials (SRM-278, RGM-1, PHM, LGB and LVC). The non-obsidian debitage (quartz, silicified conglomerate, and pottery), and the non-obsidian reference materials (agricultural soil, basalt, granite, and sediment), analyzed here are composed of materials more heterogeneous than obsidian, therefore these materials are not nearly as representative of the entire material mass from which they were taken. However, for the purposes of this study, the assumption can still be reasonably applied to these materials, as they are outside the scope of this study.

The results for the analyses obtained here for both the initial and duplicate portions for all 6 obsidian debitage pieces and 3 Supplemental Standards subjected to duplication are given in Table B-2. This table is presented on 3 pages, with each page giving the analytical results for the 2 pieces and 1 Supplemental Standard that were analyzed in a single analytical run. The very first column of each of the 3 pages of the table lists the 28 elements analyzed in each run of this study. The remaining 12 columns

Table B-2. Elemental Values (in ppm) for Select Obsidian Artifact and Other Reference Material Samples as Determined from Separate Aliquots ("Duplicate Samples").

Analytical Run 1

	Artifact CS-08				**Artifact CS-18**				**Other Reference Material LGB**			
Element	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**
Al	62440	61330	**61890**	**1.79**	62440	64670	**63560**	**3.51**	65790	63560	**64680**	**3.45**
Ba	1001	1092	**1047**	**8.70**	1001	1092	**1047**	**8.70**	1456	1365	**1411**	**6.45**
Ca	6499	6693	**6596**	**2.94**	6499	7081	**6790**	**8.57**	4947	4850	**4899**	**1.98**
Ce	51.02	48.33	**49.67**	**5.41**	49.23	51.91	**50.57**	**5.31**	53.70	51.91	**52.81**	**3.39**
Cr	167.3	167.3	**167.3**	**0.00**	200.7	223.0	**211.9**	**10.5**	434.9	423.7	**429.3**	**2.60**
Cs	8.274	8.274	**8.274**	**0.00**	8.176	8.570	**8.373**	**4.71**	3.940	3.842	**3.891**	**2.53**
Cu	55.46	247.8	**151.6**	**127**	23.60	23.60	**23.60**	**0.00**	96.76	93.22	**94.99**	**3.73**
Fe	8282	8585	**8434**	**3.59**	8686	9595	**9141**	**9.94**	8585	8888	**8737**	**3.47**
Ga	10.12	10.12	**10.12**	**0.00**	10.12	11.04	**10.58**	**8.70**	12.88	11.04	**11.96**	**15.4**
K	31320	31320	**31320**	**0.00**	31320	33480	**32400**	**6.67**	34560	31320	**32940**	**9.84**
La	31.00	28.68	**29.84**	**7.79**	29.45	31.78	**30.61**	**7.59**	30.23	29.45	**29.84**	**2.60**
Li	59.85	59.85	**59.85**	**0.00**	64.05	63.00	**63.53**	**1.65**	31.50	32.55	**32.03**	**3.28**
Mg	550.0	550.0	**550.0**	**0.00**	550.0	660.0	**605.0**	**18.2**	550.0	550.0	**550.0**	**0.00**
Mn	459.8	449.4	**454.6**	**2.30**	449.4	491.2	**470.3**	**8.89**	313.5	292.6	**303.1**	**6.90**
Na	23350	23350	**23350**	**0.00**	23350	24360	**23860**	**4.23**	27410	26390	**26900**	**3.79**
Nb	8.084	7.802	**7.943**	**3.55**	7.614	9.212	**8.413**	**19.0**	7.990	8.084	**8.037**	**1.17**
Ni	5.782	10.78	**8.281**	**60.4**	9.604	10.78	**10.19**	**11.5**	13.72	11.76	**12.74**	**15.4**
Pb	18.40	17.48	**17.94**	**5.13**	18.40	19.32	**18.86**	**4.88**	16.56	16.56	**16.56**	**0.00**
Rb	153.8	153.8	**153.8**	**0.00**	153.8	153.8	**153.8**	**0.00**	99.43	97.38	**98.40**	**2.08**
Sr	189.0	178.5	**183.8**	**5.71**	189.0	178.5	**183.8**	**5.71**	68.25	72.45	**70.35**	**5.97**
Ta	0.9450	0.8505	**0.8978**	**10.5**	0.8505	1.040	**0.9450**	**20.0**	0.7560	0.6615	**0.7088**	**13.3**
Th	12.68	11.70	**12.19**	**8.00**	12.68	12.68	**12.68**	**0.00**	9.750	9.653	**9.701**	**1.01**
Tl	1.232	1.120	**1.176**	**9.52**	1.232	1.120	**1.176**	**9.52**	0.5600	0.5600	**0.5600**	**0.00**
U	4.559	4.074	**4.317**	**11.2**	4.268	4.656	**4.462**	**8.70**	4.074	3.880	**3.977**	**4.88**
V	3.860	5.790	**4.825**	**40.0**	4.825	5.790	**5.308**	**18.2**	4.825	5.790	**5.308**	**18.2**
W	1.800	1.600	**1.700**	**11.8**	1.500	1.700	**1.600**	**12.5**	1.100	1.200	**1.150**	**8.70**
Y	15.39	15.39	**15.39**	**0.00**	14.58	16.20	**15.39**	**10.5**	25.11	24.30	**24.71**	**3.28**
Zn	42.64	68.64	**55.64**	**46.7**	37.44	37.44	**37.44**	**0.00**	39.52	37.44	**38.48**	**5.41**

Table B-2, continued. Elemental Values (in ppm) for Select Obsidian Artifact and Other Reference Material Samples as Determined from Separate Aliquots ("Duplicate Samples").

Analytical Run 2

	Artifact VT-01				Artifact VT-16				Other Reference Material PHM			
Element	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**
Al	83250	73130	**78190**	**12.9**	79880	72000	**75940**	**10.4**	69750	70880	**70320**	**1.61**
Ba	979.0	979.0	**979.0**	**0.00**	979.0	979.0	**979.0**	**0.00**	14.69	14.24	**14.46**	**3.08**
Ca	9024	9024	**9024**	**0.00**	9216	8928	**9072**	**3.17**	864.0	864.0	**864.0**	**0.00**
Ce	52.75	46.42	**49.59**	**12.8**	51.70	46.42	**49.06**	**10.8**	98.12	94.95	**96.53**	**3.28**
Cr	292.5	269.1	**280.8**	**8.33**	362.7	351.0	**356.9**	**3.28**	321.8	327.6	**324.7**	**1.80**
Cs	7.998	7.533	**7.766**	**5.99**	7.905	7.812	**7.859**	**1.18**	4.185	4.092	**4.139**	**2.25**
Cu	83.84	83.84	**83.84**	**0.00**	20.70	10.35	**15.53**	**66.7**	124.2	124.2	**124.2**	**0.00**
Fe	11110	11110	**11110**	**0.00**	11110	11110	**11110**	**0.00**	18180	19190	**18690**	**5.40**
Ga	12.32	13.20	**12.76**	**6.90**	13.20	12.32	**12.76**	**6.90**	26.84	29.04	**27.94**	**7.87**
K	39130	38220	**38680**	**2.35**	40040	39130	**39590**	**2.30**	37310	40040	**38680**	**7.06**
La	31.02	30.08	**30.55**	**3.08**	31.02	31.02	**31.02**	**0.00**	43.24	42.30	**42.77**	**2.20**
Li	67.34	65.52	**66.43**	**2.74**	67.34	65.52	**66.43**	**2.74**	62.79	63.70	**63.25**	**1.44**
Mg	868.0	744.0	**806.0**	**15.4**	868.0	868.0	**868.0**	**0.00**	372.0	372.0	**372.0**	**0.00**
Mn	553.8	521.9	**537.8**	**5.94**	564.5	511.2	**537.8**	**9.90**	1172	1278	**1225**	**8.70**
Na	28950	27990	**28470**	**3.37**	28950	28950	**28950**	**0.00**	40530	42460	**41500**	**4.65**
Nb	8.736	7.968	**8.352**	**9.20**	9.408	8.256	**8.832**	**13.0**	88.80	86.40	**87.60**	**2.74**
Ni	16.83	13.86	**15.35**	**19.4**	19.80	12.87	**16.34**	**42.4**	14.85	15.84	**15.35**	**6.45**
Pb	18.53	17.55	**18.04**	**5.41**	19.50	15.60	**17.55**	**22.2**	30.71	30.23	**30.47**	**1.60**
Rb	156.0	165.8	**160.9**	**6.06**	165.8	165.8	**165.8**	**0.00**	204.8	204.8	**204.8**	**0.00**
Sr	175.1	175.1	**175.1**	**0.00**	185.4	175.1	**180.3**	**5.71**	2.575	2.060	**2.318**	**22.2**
Ta	1.045	0.9405	**0.9928**	**10.5**	1.045	0.9405	**0.9928**	**10.5**	5.225	5.016	**5.121**	**4.08**
Th	13.59	12.54	**13.06**	**8.00**	14.63	12.54	**13.59**	**15.4**	21.95	21.95	**21.95**	**0.00**
Tl	1.278	1.065	**1.172**	**18.2**	1.172	1.065	**1.118**	**9.52**	1.065	1.172	**1.118**	**9.52**
U	4.693	3.829	**4.261**	**20.3**	4.940	3.582	**4.261**	**31.9**	8.213	8.151	**8.182**	**0.75**
V	4.020	4.020	**4.020**	**0.00**	4.020	5.025	**4.523**	**22.2**	6.030	7.035	**6.533**	**15.4**
W	1.900	1.700	**1.800**	**11.1**	1.900	1.600	**1.750**	**17.1**	1.050	1.000	**1.025**	**4.88**
Y	17.00	17.00	**17.00**	**0.00**	17.00	17.00	**17.00**	**0.00**	119.0	119.0	**119.0**	**0.00**
Zn	51.84	50.76	**51.30**	**2.11**	44.28	37.80	**41.04**	**15.8**	259.2	270.0	**264.6**	**4.08**

Table B-2, continued. Elemental Values (in ppm) for Select Obsidian Artifact and Other Reference Material Samples as Determined from Separate Aliquots ("Duplicate Samples").

Analytical Run 3

	Artifact MO-03				Artifact VT-15				Other Reference Material LVC			
Element	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**	**Aliquot 1 Value**	**Aliquot 2 Value**	**Mean Value**	**Range of Values (%)**
Al	*>70000*	73100	**73100**	**--**	*>70000*	73100	**73100**	**--**	70950	*>70000*	**70950**	**--**
Ba	1010	1010	**1010**	**0.00**	1212	1010	**1111**	**18.2**	974.7	1212	**1093**	**21.7**
Ca	9400	8600	**9000**	**8.89**	11000	9000	**10000**	**20.0**	5250	6300	**5775**	**18.2**
Ce	55.75	50.18	**52.96**	**10.5**	62.44	50.18	**56.31**	**21.8**	65.23	69.13	**67.18**	**5.81**
Cr	343.0	343.0	**343.0**	**0.00**	404.3	318.5	**361.4**	**23.7**	471.6	465.5	**468.6**	**1.31**
Cs	8.080	7.575	**7.828**	**6.45**	9.191	7.676	**8.434**	**18.0**	4.899	5.959	**5.429**	**19.5**
Cu	70.29	82.17	**76.23**	**15.6**	43.56	39.60	**41.58**	**9.52**	133.7	178.2	**155.9**	**28.6**
Fe	9550	9550	**9550**	**0.00**	13370	9550	**11460**	**33.3**	11460	13370	**12420**	**15.4**
Ga	14.00	12.00	**13.00**	**15.4**	15.00	12.00	**13.50**	**22.2**	14.50	18.00	**16.25**	**21.5**
K	39200	37190	**38200**	**5.26**	44220	39200	**41710**	**12.0**	42210	53270	**47740**	**23.2**
La	32.16	29.15	**30.65**	**9.84**	35.18	30.15	**32.66**	**15.4**	39.20	43.22	**41.21**	**9.76**
Li	70.73	62.53	**66.63**	**12.3**	76.88	64.58	**70.73**	**17.4**	36.90	45.10	**41.00**	**20.0**
Mg	815.5	699.0	**757.3**	**15.4**	932.0	699.0	**815.5**	**28.6**	699.0	815.5	**757.3**	**15.4**
Mn	519.8	482.0	**500.9**	**7.55**	585.9	491.4	**538.7**	**17.5**	236.3	330.8	**283.5**	**33.3**
Na	28500	26600	**27550**	**6.90**	31350	27550	**29450**	**12.9**	28500	35150	**31830**	**20.9**
Nb	10.14	8.580	**9.360**	**16.7**	11.70	8.580	**10.14**	**30.8**	17.55	17.94	**17.75**	**2.20**
Ni	12.12	19.19	**15.66**	**45.2**	16.16	14.14	**15.15**	**13.3**	18.18	40.40	**29.29**	**75.9**
Pb	19.35	17.20	**18.28**	**11.8**	21.50	22.58	**22.04**	**4.88**	26.34	30.10	**28.22**	**13.3**
Rb	170.3	147.6	**158.9**	**14.3**	181.6	158.9	**170.3**	**13.3**	141.9	158.9	**150.4**	**11.3**
Sr	190.5	177.8	**184.2**	**6.90**	254.0	177.8	**215.9**	**35.3**	90.81	109.2	**100.0**	**18.4**
Ta	1.152	0.9600	**1.056**	**18.2**	1.248	1.056	**1.152**	**16.7**	1.392	1.536	**1.464**	**9.84**
Th	13.38	12.27	**12.82**	**8.70**	14.50	13.38	**13.94**	**8.00**	16.73	18.96	**17.84**	**12.5**
Tl	1.220	1.098	**1.159**	**10.5**	1.342	1.220	**1.281**	**9.52**	0.8540	1.098	**0.9760**	**25.0**
U	4.795	4.237	**4.516**	**12.3**	5.464	4.126	**4.795**	**27.9**	6.077	6.133	**6.105**	**0.91**
V	4.700	4.700	**4.700**	**0.00**	4.700	4.700	**4.700**	**0.00**	6.463	8.225	**7.344**	**24.0**
W	1.800	1.700	**1.750**	**5.71**	2.100	1.800	**1.950**	**15.4**	2.300	3.000	**2.650**	**26.4**
Y	17.64	15.68	**16.66**	**11.8**	19.60	16.66	**18.13**	**16.2**	15.19	17.64	**16.42**	**14.9**
Zn	51.75	51.75	**51.75**	**0.00**	51.75	45.00	**48.38**	**14.0**	57.38	76.50	**66.94**	**28.6**

on each page are divided evenly between the 3 duplicate samples for that analytical run, thus 4 columns per duplicate sample. The first 2 columns for a given duplicate sample contain the analytical results for both digestion aliquots (both duplicate samples), and are labeled as "Aliquot 1" and "Aliquot 2." The third column for each duplicate sample contains the calculated arithmetic mean of these 2 values ("Mean Value"), and the fourth column for each duplicate sample presents the range between the two Aliquot Values as a percentage ("Range of Values"). Aliquot 1 Values, Aliquot 2 Values, and Mean Values are all presented in 4 significant digits. The Range of Values (as a percent) for each duplicate sample is calculated using the following equation, and presented in 3 significant digits:

$$\text{Percent Range of Values} = \frac{(\text{Maximum Value} - \text{Minimum Value})}{(\text{Mean Value})} \times 100$$

This quantity represents how much variation exists between the 2 data points (the two Aliquot Values). For example, on the first page of Table B-2, artifact (obsidian debitage piece) CS-08 (Analytical Run 1) is shown to have a Ca value determined to be within ± 2.94% of the Mean Value of 6596 ppm. This means that any further analyses of Ca conducted on this piece would be expected to yield analytical values within the range of 6596 ppm ± 1.47% (6596 ppm -1.47% to 6596 ppm +1.47%), or 6499 ppm to 6693 ppm.

Quite a few of the 9 duplicates reveal a largish variation in the percent Range of Values for Cu, varying from as low as 0.00% (CS-18, VT-01 and PHM) and 3.73% (LGB), to 9.52% (VT-15), 15.6% (MO-03), 28.6% (LVC), 66.7% (VT-16), and the highest, 127% (CS-08). This largish variation in the Range of Values appears to occur for Ni also, varying from as low as 6.45% (PHM), to 11.5% (CS-18), 13.3% (VT-15), 15.4% (LGB), 19.4% (VT-01), 42.4% (VT-16), 45.2% (MO-03), 60.4% (CS-08), and the highest, 75.9% (LVC). No other elements appear to show such consistently large Ranges of Values across the spectrum of duplicates, although some elements show largish Ranges of Values in some runs, or for some duplicates, but not others. As an example, V: (in Run 1) 40.0% for CS-08, and 18.2% for both CS-18 and LGB, (in Run 2) 0.00% for VT-01, 22.2% for VT-16, and 15.4% for PHM, and (in Run 3) 0.00% for both MO-03 and VT-15, and 24.0% for LVC. For another example, Zn: (in Run 1) 46.7% for CS-08, 0.00% for CS-18, and 5.41% for LGB, (in Run 2) 2.11% for VT-01, 15.8% for VT-16, and 4.08% for PHM, and (in Run 3) 0.00% for MO-03, 14.0% for VT-15, and 28.6% for LVC. One plausible explanation for such possibly inconsistent variations seen in the Ranges of Values may be that there are larger variations in the compositions of these materials than anticipated, based on how well-homogenized their powders had been. Another plausible explanation may be that these (and other) elements may have been more problematic to measure by the ICP-MS during the actual running conditions experienced for these particular analytical runs than usually anticipated.

One definite pattern is that the percent Range of Values for all 3 duplicates in Run 3 are consistently high, with a few exceptions. This seems consistent with information provided by the USGS analyst who performed all three analytical runs, which was that the instrument was a bit behind in the regular cleaning schedule when this particular run was performed (Allen Meier, verbal communication 4/22/1999). An instrument in need of cleaning when a run was performed would undoubtedly result in higher variations in values obtained, just as seen here in the overall higher Range of Values for this run.

Repeat Measurements. As detailed earlier, a “repeat” measurement consists of a second analytical measurement of the composition of a given digested sample portion. These repeat analyses were performed during the same analytical run, and on the same digested sample portion as the first measurement. Repeat analyses were performed here for 2 reasons: 1) they are routinely performed on certain sample aliquots as part of the instrumental protocol, to maintain instrument performance during the analytical run (Allen Meier, verbal communication 1/12/1999); and, 2) selected artifact samples, plus the 3 Supplemental Standards, were repeated here to gain more information about these materials. The repeats performed here as part of the instrumental protocol during each of the 3 analytical runs included all 3 blanks, all 6 standards formerly categorized as Primary Standards (SRM-278, RGM-1, BCR-1, BHVO-1, SRM-2709, and GSD-5), and both standards formerly categorized as Secondary Standards (PPG and SJS), as well as the 1st non-reference sample of each run, and every 10th such sample thereafter of each run (CS-02, CS-15, CS-25 and LP-01 in Run 1; CS-06, MO-02, VT-10 and VT-

23 in Run 2; and CS-01, VT-02, VT-31 and VT-41 in Run 3). The repeat analyses performed on other single digestion aliquots were performed on the very lowest mass obsidian debitage samples (CS-07 and CS-11 in Run 1; and CS-01, VT-35, VT-36, VT-37, VT-38 and VT-42 in Run 3), and all 3 Supplementary Standards (LGB in Run 1, PHM in Run 2, and LVC in Run 3). The very lowest mass debitage pieces were those with such small masses that the entire sample was used in obtaining the one aliquot available for analysis for each. As no powdered sample remained of these samples, performing repeat analyses on the one and only digestion aliquots made from these samples was extremely desirable to gain as much information as possible for these lowest mass artifacts. Repeat analyses were performed on the digestion aliquots of 3 Supplementary Standards to obtain more information on these materials for which little or no information was available.

Information regarding the repeated measurements performed on certain aliquots of standards samples was unavailable to this author for examination separate from the first measurements on these aliquots. This included all of the standards in Run 1, as the two values for each had been inadvertently averaged together prior to presentation to the author of this study, thus were presented as single values. The repeated measurements for all of the standards in the 2 subsequent runs were available for separate examination. The first and repeated measurements for each standard for each of Runs 2 and 3 were examined, the arithmetic means for each of these 2 values for each of those two runs calculated, and then presented here as single values for each ("Run 2 Value" and "Run 3 Value"). However, any repeated measurement values below detection limits (such as "<500 ppm" for Ca in PHM in Run 1 in Table B-5) were not included in the calculations of the means, either when determining the single run values (as just mentioned) or the overall Mean Values for all 3 runs. See Tables B-3 through B-30 at the end of this Appendix for the standards data.

The first and repeated measurements for all 19 of the obsidian debitage samples upon which repeat measurements had been performed were available for examination by this author. These values for these pieces were examined in the same manner as the standards had been, and are presented in Table C-1 (Appendix C) as the arithmetic means of the 2 measurements for all of these artifacts, except four. These 4 pieces (CS-07 in

Run 1; and VT-35, VT-36 and VT-42 in Run 3) constitute half of the 8 lowest mass obsidian debitage pieces. The repeated measurements for these 4 pieces were so noticeably different from the first measurements (all 4 of the repeated measurements were substantially lower in value than the first measurements), that all these data for all 19 of these pieces (and every standard, and all other debitage pieces, as well) were all carefully double- and triple-checked. In theory, there should not have been such large differences between supposedly identical measurements made on the exact same liquid. However, as this is what occurred, and there appeared to be a distinct pattern with the repeat measurements being substantially lower, this researcher decided to take the first measurements for each of these 4 pieces as the more plausible. Therefore, the repeated measurements for these 4 low-weight obsidian debitage samples (CS-07 in Run 1; and VT-35, VT-36 and VT-42 in Run 3), with the very different values from the first measurements, were discarded from the data set for each run. Thus, the values for these 4 artifacts presented in Table C-1 (Appendix C) are the first measurements, and not the arithmetic means of the 2 measurements.

The data obtained here from the repeated measurements performed on single aliquots was not used for determining precision in this study. It was decided by this researcher that due to the problem(s) associated with this type of information as obtained for this particular data set, as noted immediately above, this information may not be entirely reliable. Therefore, the data presented in Table B-2, that of duplicate measurements obtained from two separate digestion aliquots from 2 separate portions of the same powdered sample, was deemed as being the more reliable and thus more usable in this context.

Table B-3. Aluminum (Al) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	74900[a, b]	73600	67500	74200	71800	-4.14
Rhyolite Obsidian	RGM-1	72500[b, c]	73600	79300	73100	75300	3.86
Supplemental:							
Obsidian	PHM	--	55800	70300	61800	62600	--
Obsidian	LGB	--	64700	75900	68800	69800	--
Obsidian	LVC	--	68000	80400	71000	73100	--
Additional:							
Granite	PPG	70000[d]	82500	78200	--	80400	14.86
Basalt	BCR-1	72190[b]	83600	78800	73600	78700	9.02
Basalt	BHVO-1	73040[b, e]	79200	82700	68800	76900	5.28
Soil	SRM-2709	75000[b]	84700	82100	71000	79300	5.73
Soil	GSD-5	81350[b, f]	> *80000*	86600	> *70000*	86600	6.45
Soil	SJS	80000[d]	> *80000*	87800	76300	82100	2.63

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[e] USGS Certificate of Analysis for BHVO-1 (1995).

[f] Xie, Yan, Li and Shen (1985).

Table B-4. Barium (Ba) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	881[a]	892	868	889	883	0.23
Rhyolite Obsidian	RGM-1	810[b, c]	801	819	808	809	-0.12
Supplemental:							
Obsidian	PHM	30[d]	14.6	14.5	12.1	13.7	-54.33
Obsidian	LGB	1270[d]	1410	1290	1310	1340	5.51
Obsidian	LVC	--	1000	979	1090	1020	--
Additional:							
Granite	PPG	680[e]	646	650	--	648	-4.71
Basalt	BCR-1	681[c]	655	663	667	662	-2.79
Basalt	BHVO-1	139[c, f]	118	138	111	122	-12.23
Soil	SRM-2709	968[c, g]	901	877	899	892	-7.85
Soil	GSD-5	440[c, h]	410	396	424	410	-6.82
Soil	SJS	880[e]	837	837	879	851	-3.30

[a] Glascock, Elam and Cobean (1988). Although Govindaraju (1994) reported an SRM-278 barium value of 1140 ppm, Glascock, Elam and Cobean's (1988) reported value of 881 ppm is used here as it is significantly closer to the values obtained in this study. Also, their value was obtained using only INAA, a method with high precision, while Govindaraju's (1994) values are composites from numerous analytical methods.

[b] USGS Certificate of Analysis for RGM-1 (1995).

[c] Govindaraju (1994).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-5. Calcium (Ca) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	7030[a, b]	7280	6860	7000	7050	0.28
Rhyolite Obsidian	RGM-1	8220[b, c]	7950	8450	8300	8230	0.12
Supplemental:							
Obsidian	PHM	--	*< 500*	864	850	857	--
Obsidian	LGB	--	4900	6140	6100	5710	--
Obsidian	LVC	--	3880	5470	5780	5040	--
Additional:							
Granite	PPG	14000[d]	15500	14400	--	15000	7.14
Basalt	BCR-1	49700[b]	49500	47000	46500	47700	-4.02
Basalt	BHVO-1	81470[b, e]	76600	80200	74500	77100	-5.36
Soil	SRM-2709	18900[b, f]	19400	18200	18500	18700	-1.06
Soil	GSD-5	38200[b, g]	39800	35500	38500	37900	-0.79
Soil	SJS	22000[d]	23300	20200	22000	21800	-0.91

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[e] USGS Certificate of Analysis for BHVO-1 (1995).

[f] NIST Certificate of Analysis for SRM-2709 (1993).

[g] Xie, Yan, Li and Shen (1985).

Table B-6. Cerium (Ce) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	62.2[a, b]	62.7	55.9	62.4	60.3	-3.05
Rhyolite Obsidian	RGM-1	47[b, c]	46.5	51.7	46.8	48.3	2.77
Supplemental:							
Obsidian	PHM	92.0[d]	98.5	96.5	97.6	97.5	5.98
Obsidian	LGB	48.4[d]	52.8	51.2	54.1	52.7	8.88
Obsidian	LVC	--	63.5	65.4	67.2	65.4	--
Additional:							
Granite	PPG	270[e]	286	280	--	283	4.81
Basalt	BCR-1	53.7[b]	52.8	60.7	58.5	57.3	6.70
Basalt	BHVO-1	39[b, f]	34.9	45.9	40.1	40.3	3.33
Soil	SRM-2709	42[b, g]	41.2	49.1	46.3	45.5	8.33
Soil	GSD-5	89[b, h]	79.7	92.3	93.1	88.4	-0.67
Soil	SJS	45[e]	44.8	50.6	53.5	49.6	10.22

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-7. Chromium (Cr) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	6.1[a, b]	6.69	6.44	6.13	6.42	5.25
Rhyolite Obsidian	RGM-1	3.7[b, c]	3.35	3.51	3.68	3.51	-5.14
Supplemental:							
Obsidian	PHM	--	279	325	306	303	--
Obsidian	LGB	--	429	509	545	494	--
Obsidian	LVC	--	368	410	469	416	--
Additional:							
Granite	PPG	10[d]	10.0	11.1	--	10.6	6.00
Basalt	BCR-1	16[b]	12.3	13.5	14.1	13.3	-16.88
Basalt	BHVO-1	289[b]	323	357	319	333	15.22
Soil	SRM-2709	130[b, e]	123	129	132	128	-1.54
Soil	GSD-5	70[b, f]	75.8	77.8	81.5	78.4	12.00
Soil	SJS	120[d]	123	123	129	125	4.17

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[e] NIST Certificate of Analysis for SRM-2709 (1993).

[f] Xie, Yan, Li and Shen (1985).

Table B-8. Cesium (Cs) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	5.5 [a, b]	5.32	5.16	5.20	5.23	-4.91
Rhyolite Obsidian	RGM-1	9.6 [b, c]	9.85	10.2	10.1	10.1	5.21
Supplemental:							
Obsidian	PHM	3.92 [d]	4.53	4.14	4.04	4.24	8.16
Obsidian	LGB	3.40 [d]	3.89	3.63	3.48	3.67	7.94
Obsidian	LVC	--	5.42	5.16	5.43	5.34	--
Additional:							
Granite	PPG	--	1.77	1.81	--	1.79	--
Basalt	BCR-1	0.96 [b]	0.985	1.02	0.960	0.988	2.92
Basalt	BHVO-1	0.13 [b, e]	*< 0.1*	0.0930	0.101	0.0970	-25.38
Soil	SRM-2709	5.3 [b, f]	5.71	5.67	5.50	5.63	6.23
Soil	GSD-5	9.4 [b, g]	9.26	8.84	8.99	9.03	-3.94
Soil	SJS	--	6.21	6.00	6.26	6.16	--

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] USGS Certificate of Analysis for BHVO-1 (1995).

[f] NIST Certificate of Analysis for SRM-2709 (1993).

[g] Xie, Yan, Li and Shen (1985).

Table B-9. Copper (Cu) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	5.9 [a, b]	< 3	6.73	6.93	6.83	15.76
Rhyolite Obsidian	RGM-1	12 [b, c]	7.08	10.4	9.90	9.13	-23.92
Supplemental:							
Obsidian	PHM	--	153	124	104	127	--
Obsidian	LGB	--	95.0	76.1	109	93.4	--
Obsidian	LVC	--	177	160	156	164	--
Additional:							
Granite	PPG	11 [d]	7.08	10.4	--	8.74	-20.55
Basalt	BCR-1	19 [b]	11.8	20.7	9.90	14.1	-25.79
Basalt	BHVO-1	136 [b, e]	153	145	114	137	0.74
Soil	SRM-2709	34.6 [b, f]	40.1	35.7	30.2	35.3	2.02
Soil	GSD-5	137 [b, g]	177	140	129	149	8.76
Soil	SJS	40 [d]	47.2	40.9	36.1	41.4	3.50

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[e] USGS Certificate of Analysis for BHVO-1 (1995).

[f] NIST Certificate of Analysis for SRM-2709 (1993).

[g] Xie, Yan, Li and Shen (1985).

Table B-10. Iron (Fe) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	14300[a, b]	14100	14600	13800	14200	-0.70
Rhyolite Obsidian	RGM-1	13000[b, c]	13100	12600	13400	13000	0.00
Supplemental:							
Obsidian	PHM	15800[d]	17200	18700	20100	18700	18.35
Obsidian	LGB	6200[d]	8740	9900	8360	9000	45.16
Obsidian	LVC	--	11100	12100	12400	11900	--
Additional:							
Granite	PPG	27000[e]	29300	26800	--	28100	4.07
Basalt	BCR-1	93790[b]	97000	92400	101000	96800	3.21
Basalt	BHVO-1	85540[b, f]	84800	87900	89300	87300	2.06
Soil	SRM-2709	35000[b, g]	38400	34300	36800	36500	4.29
Soil	GSD-5	41000[b, h]	43400	39400	43900	42200	2.93
Soil	SJS	39000[e]	42400	37900	41500	40600	4.10

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-11. Gallium (Ga) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	13[a]	16.6	16.3	16.5	16.5	26.92
Rhyolite Obsidian	RGM-1	15[a, b]	14.7	15.0	15.0	14.9	-0.67
Supplemental:							
Obsidian	PHM	--	25.8	27.9	28.0	27.2	--
Obsidian	LGB	--	12.0	12.8	13.5	12.8	--
Obsidian	LVC	--	12.9	14.5	16.3	14.6	--
Additional:							
Granite	PPG	23[c]	23.0	22.0	--	22.5	-2.17
Basalt	BCR-1	22[a]	21.2	20.2	20.5	20.6	-6.36
Basalt	BHVO-1	21[a, d]	19.3	20.7	19.5	19.8	-5.71
Soil	SRM-2709	14[a, e]	15.6	14.5	15.5	15.2	8.57
Soil	GSD-5	20.3[a, f]	18.4	18.0	19.0	18.5	-8.87
Soil	SJS	18[c]	17.5	16.3	18.0	17.3	-3.89

[a] Govindaraju (1994).

[b] USGS Certificate of Analysis for RGM-1 (1995).

[c] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[d] USGS Certificate of Analysis for BHVO-1 (1995).

[e] NIST Certificate of Analysis for SRM-2709 (1993).

[f] Xie, Yan, Li and Shen (1985).

Table B-12. Potassium (K) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	34500 [a, b]	33500	34600	34200	34100	-1.16
Rhyolite Obsidian	RGM-1	35700 [b, c]	36700	35500	36200	36100	1.12
Supplemental:							
Obsidian	PHM	37800 [d]	35600	38700	36700	37000	-2.12
Obsidian	LGB	35200 [d]	32900	36400	34700	34700	-1.42
Obsidian	LVC	--	41000	44100	47700	44300	--
Additional:							
Granite	PPG	44000 [e]	49700	43700	--	46700	6.14
Basalt	BCR-1	14000 [b]	15100	13200	13100	13800	-1.43
Basalt	BHVO-1	4300 [b, f]	4320	4100	4070	4160	-3.26
Soil	SRM-2709	20300 [b, g]	22700	18700	19100	20200	-0.49
Soil	GSD-5	17400 [b, h]	19400	15900	17600	17600	1.15
Soil	SJS	19000 [e]	21600	17700	19100	19500	2.63

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-13. Lanthanum (La) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	32 [a]	31.8	28.2	31.7	30.6	-4.38
Rhyolite Obsidian	RGM-1	24 [a, b]	24.0	26.8	24.1	25.0	4.17
Supplemental:							
Obsidian	PHM	38.6 [c]	43.4	42.8	41.7	42.6	10.36
Obsidian	LGB	25.8 [c]	29.8	28.7	29.1	29.2	13.18
Obsidian	LVC	--	39.5	40.0	41.2	40.2	--
Additional:							
Granite	PPG	150 [d]	140	136	--	138	-8.00
Basalt	BCR-1	24.9 [a]	26.4	29.6	28.1	28.0	12.45
Basalt	BHVO-1	16 [a, e]	14.7	18.8	17.1	16.9	5.62
Soil	SRM-2709	23 [a, f]	21.7	24.9	23.6	23.4	1.74
Soil	GSD-5	46 [a, g]	34.1	43.2	41.7	39.7	-13.70
Soil	SJS	24 [d]	24.0	25.9	26.6	25.5	6.25

[a] Govindaraju (1994).

[b] USGS Certificate of Analysis for RGM-1 (1995).

[c] Glascock (1999).

[d] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[e] USGS Certificate of Analysis for BHVO-1 (1995).

[f] NIST Certificate of Analysis for SRM-2709 (1993).

[g] Xie, Yan, Li and Shen (1985).

Table B-14. Lithium (Li) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	--	41.0	40.5	43.1	41.5	--
Rhyolite Obsidian	RGM-1	57 [a, b]	56.7	57.3	57.4	57.1	0.18
Supplemental:							
Obsidian	PHM	--	62.0	63.2	64.1	63.1	--
Obsidian	LGB	--	32.0	32.3	32.8	32.4	--
Obsidian	LVC	--	34.7	36.4	41.0	37.4	--
Additional:							
Granite	PPG	30 [c]	30.5	29.6	--	30.1	0.33
Basalt	BCR-1	12.9 [b]	13.7	12.7	12.3	12.9	0.00
Basalt	BHVO-1	4.6 [b, d]	5.25	4.78	4.61	4.88	6.09
Soil	SRM-2709	--	55.7	52.3	52.3	53.4	--
Soil	GSD-5	45 [b, e]	46.2	42.8	45.1	44.7	-0.67
Soil	SJS	69 [c]	73.5	62.8	67.1	67.8	-1.74

[a] USGS Certificate of Analysis for RGM-1 (1995).

[b] Govindaraju (1994).

[c] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[d] USGS Certificate of Analysis for BHVO-1 (1995).

[e] Xie, Yan, Li and Shen (1985).

Table B-15. Magnesium (Mg) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	1400[a, b]	1540	1360	1460	1450	3.57
Rhyolite Obsidian	RGM-1	1700[b, c]	1540	1740	1630	1640	-3.53
Supplemental:							
Obsidian	PHM	--	220	372	350	314	--
Obsidian	LGB	--	550	682	641	624	--
Obsidian	LVC	--	550	806	757	704	--
Additional:							
Granite	PPG	5000[d]	5500	5020	--	5260	5.20
Basalt	BCR-1	21000[b]	25300	24800	24500	24900	18.57
Basalt	BHVO-1	43600[b, e]	47300	53300	50100	50200	15.14
Soil	SRM-2709	15100[b, f]	17600	18600	17500	17900	18.54
Soil	GSD-5	5900[b, g]	6710	6260	6060	6340	7.46
Soil	SJS	15000[d]	17600	17400	18600	17900	19.33

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[e] USGS Certificate of Analysis for BHVO-1 (1995).

[f] NIST Certificate of Analysis for SRM-2709 (1993).

[g] Xie, Yan, Li and Shen (1985).

Table B-16. Manganese (Mn) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	400[a, b]	397	383	354	378	-5.50
Rhyolite Obsidian	RGM-1	280[b, c]	282	293	312	296	5.71
Supplemental:							
Obsidian	PHM	1149[d]	1050	1220	992	1090	-5.13
Obsidian	LGB	327[d]	303	357	312	324	-0.92
Obsidian	LVC	--	272	314	284	290	--
Additional:							
Granite	PPG	670[e]	742	714	--	728	8.66
Basalt	BCR-1	1400[b]	1460	1540	1280	1430	2.14
Basalt	BHVO-1	1300[b, f]	1360	1490	1130	1330	2.31
Soil	SRM-2709	538[b, g]	596	570	487	551	2.42
Soil	GSD-5	1160[b, h]	1250	1220	1040	1170	0.86
Soil	SJS	540[e]	596	564	506	555	2.78

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-17. Sodium (Na) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	35900 [a, b]	35500	36700	35600	35900	0.00
Rhyolite Obsidian	RGM-1	30200 [b, c]	30500	29400	30400	30100	-0.33
Supplemental:							
Obsidian	PHM	38000 [d]	35500	41500	38000	38300	0.79
Obsidian	LGB	28400 [d]	26900	30900	29000	28900	1.76
Obsidian	LVC	--	26400	29900	31800	29400	--
Additional:							
Granite	PPG	23000 [e]	26400	24100	--	25300	10.00
Basalt	BCR-1	24300 [b]	27400	24100	23300	24900	2.47
Basalt	BHVO-1	16800 [b, f]	17300	17400	16200	17000	1.19
Soil	SRM-2709	11600 [b, g]	12200	11600	11400	11700	0.86
Soil	GSD-5	3000 [b, h]	2940	2560	2660	2720	-9.33
Soil	SJS	11000 [e]	12200	10100	10900	11100	0.91

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-18. Niobium (Nb) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	18[a]	17.9	16.8	17.2	17.3	-3.89
Rhyolite Obsidian	RGM-1	8.9[a, b]	8.93	9.50	9.36	9.26	4.04
Supplemental:							
Obsidian	PHM	--	81.8	87.6	89.7	86.4	--
Obsidian	LGB	--	8.04	8.30	8.19	8.18	--
Obsidian	LVC	--	16.9	16.3	17.7	17.0	--
Additional:							
Granite	PPG	32[c]	59.2	65.3	--	62.3	94.69
Basalt	BCR-1	14[a]	11.3	13.0	12.5	12.3	-12.14
Basalt	BHVO-1	19[a, d]	18.8	21.1	19.9	19.9	4.74
Soil	SRM-2709	--	10.3	9.41	9.75	9.82	--
Soil	GSD-5	19[a, e]	16.9	14.9	16.8	16.2	-14.74
Soil	SJS	7[c]	10.3	10.6	11.3	10.7	52.86

[a] Govindaraju (1994).

[b] USGS Certificate of Analysis for RGM-1 (1995).

[c] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[d] USGS Certificate of Analysis for BHVO-1 (1995).

[e] Xie, Yan, Li and Shen (1985).

Table B-19. Nickel (Ni) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	3.6 [a, b]	3.53	3.61	3.59	3.58	-0.56
Rhyolite Obsidian	RGM-1	4.4 [b]	1.96	1.93	2.32	2.07	-52.95
Supplemental:							
Obsidian	PHM	--	14.7	15.3	13.1	14.4	--
Obsidian	LGB	--	12.7	13.4	15.2	13.8	--
Obsidian	LVC	--	18.6	20.3	29.3	22.7	--
Additional:							
Granite	PPG	4 [c]	3.04	3.07	--	3.06	-23.50
Basalt	BCR-1	13 [b]	9.80	9.75	9.34	9.63	-25.92
Basalt	BHVO-1	121 [b]	118	119	116	118	-2.48
Soil	SRM-2709	88 [b, d]	86.2	78.2	79.3	81.2	-7.73
Soil	GSD-5	34 [b, e]	38.2	35.1	36.9	36.7	7.94
Soil	SJS	73 [c]	76.4	69.3	73.2	73.0	0.00

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[d] NIST Certificate of Analysis for SRM-2709 (1993).

[e] Xie, Yan, Li and Shen (1985).

Table B-20. Lead (Pb) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	16.4[a, b]	16.6	15.6	16.7	16.3	-0.61
Rhyolite Obsidian	RGM-1	24[b, c]	23.9	25.4	23.7	24.3	1.25
Supplemental:							
Obsidian	PHM	--	31.3	30.5	29.0	30.3	--
Obsidian	LGB	--	16.6	16.6	16.7	16.6	--
Obsidian	LVC	--	26.7	27.3	28.2	27.4	--
Additional:							
Granite	PPG	28[d]	33.1	34.6	--	33.9	21.07
Basalt	BCR-1	13.6[b]	13.8	15.1	13.4	14.1	3.68
Basalt	BHVO-1	2.6[b, e]	1.75	2.63	2.10	2.16	-16.92
Soil	SRM-2709	18.9[b, f]	18.4	19.5	18.8	18.9	0.00
Soil	GSD-5	112[b, g]	110	117	112	113	0.89
Soil	SJS	17[d]	17.5	18.5	17.7	17.9	5.29

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[e] USGS Certificate of Analysis for BHVO-1 (1995).

[f] NIST Certificate of Analysis for SRM-2709 (1993).

[g] Xie, Yan, Li and Shen (1985).

Table B-21. Rubidium (Rb) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	127.5 [a, b]	123	122	131	125	-1.96
Rhyolite Obsidian	RGM-1	150 [b, c]	154	156	148	153	2.00
Supplemental:							
Obsidian	PHM	192 [d]	205	205	193	201	4.69
Obsidian	LGB	95 [d]	98.4	97.5	98.2	98.0	3.16
Obsidian	LVC	--	144	151	150	148	--
Additional:							
Granite	PPG	207 [e]	215	210	--	213	2.90
Basalt	BCR-1	47.2 [b]	49.2	49.7	49.9	49.6	5.08
Basalt	BHVO-1	11 [b, f]	9.33	10.7	9.36	9.80	-10.91
Soil	SRM-2709	96 [b, g]	95.3	94.6	95.9	95.3	-0.73
Soil	GSD-5	118 [b, h]	123	117	125	122	3.39
Soil	SJS	96 [e]	103	102	100	102	6.25

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-22. Strontium (Sr) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	63.5 [a, b]	68.3	61.8	66.0	65.4	2.99
Rhyolite Obsidian	RGM-1	110 [b, c]	102	113	105	107	-2.73
Supplemental:							
Obsidian	PHM	--	2.10	2.32	2.54	2.32	--
Obsidian	LGB	78 [d]	70.4	69.5	71.1	70.3	-9.87
Obsidian	LVC	--	89.3	90.1	100	93.1	--
Additional:							
Granite	PPG	230 [e]	252	237	--	245	6.52
Basalt	BCR-1	330 [b]	357	355	406	373	13.03
Basalt	BHVO-1	403 [b, f]	410	443	470	441	9.43
Soil	SRM-2709	231 [b, g]	252	237	254	248	7.36
Soil	GSD-5	204 [b, h]	221	211	241	224	9.80
Soil	SJS	240 [e]	252	247	267	255	6.25

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-23. Tantalum (Ta) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	1.2 [a, b]	1.32	1.15	1.25	1.24	3.33
Rhyolite Obsidian	RGM-1	0.95 [b, c]	0.851	0.993	0.912	0.919	-3.26
Supplemental:							
Obsidian	PHM	4.87 [d]	4.54	5.12	5.33	5.00	2.67
Obsidian	LGB	0.66 [d]	0.709	0.679	0.672	0.687	4.09
Obsidian	LVC	--	1.51	1.41	1.46	1.46	--
Additional:							
Granite	PPG	< 40 [e]	3.21	3.45	--	3.33	--
Basalt	BCR-1	0.81 [b]	0.756	0.888	0.816	0.820	1.23
Basalt	BHVO-1	1.23 [b, f]	1.13	1.41	1.34	1.29	4.88
Soil	SRM-2709	--	0.945	0.941	0.912	0.933	--
Soil	GSD-5	1.4 [b, g]	1.32	1.20	1.20	1.24	-11.43
Soil	SJS	< 40 [e]	0.945	1.05	1.20	1.07	--

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] Xie, Yan, Li and Shen (1985).

Table B-24. Thorium (Th) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	12.4[a, b]	12.7	11.0	12.8	12.2	-1.61
Rhyolite Obsidian	RGM-1	15[b, c]	14.6	16.7	14.5	15.3	2.00
Supplemental:							
Obsidian	PHM	17.9[d]	20.5	21.9	21.2	21.2	18.44
Obsidian	LGB	8.48[d]	9.70	9.77	9.64	9.70	14.39
Obsidian	LVC	--	16.6	17.8	17.8	17.4	--
Additional:							
Granite	PPG	31[e]	31.2	33.4	--	32.3	4.19
Basalt	BCR-1	5.98[b]	6.24	7.16	6.47	6.62	10.70
Basalt	BHVO-1	1.1[b, f]	1.17	1.62	1.28	1.36	23.64
Soil	SRM-2709	11[b, g]	10.7	12.0	12.1	11.6	5.45
Soil	GSD-5	15.2[b, h]	14.6	16.2	16.2	15.7	3.29
Soil	SJS	12[e]	11.7	13.6	13.4	12.9	7.50

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

Table B-25. Thallium (Tl) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	0.54[a, b]	0.560	0.586	0.549	0.565	4.63
Rhyolite Obsidian	RGM-1	0.93[b]	0.896	0.852	0.915	0.888	-4.52
Supplemental:							
Obsidian	PHM	--	1.23	1.12	1.16	1.17	--
Obsidian	LGB	--	0.560	0.533	0.549	0.547	--
Obsidian	LVC	--	1.01	0.959	0.976	0.982	--
Additional:							
Granite	PPG	--	0.896	0.852	--	0.874	--
Basalt	BCR-1	0.3[b]	0.336	0.373	0.366	0.358	19.33
Basalt	BHVO-1	0.058[b]	*< 0.1*	*< 0.1*	*< 0.1*	*< 0.1*	--
Soil	SRM-2709	0.74[b, c]	0.672	0.586	0.610	0.623	-15.81
Soil	GSD-5	1.16[b, d]	1.12	1.01	1.28	1.14	-1.72
Soil	SJS	--	0.560	0.533	0.610	0.568	--

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] NIST Certificate of Analysis for SRM-2709 (1993).

[d] Xie, Yan, Li and Shen (1985).

Table B-26. Uranium (U) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	4.58[a, b]	4.66	3.58	4.68	4.31	-5.90
Rhyolite Obsidian	RGM-1	5.8[b, c]	5.72	7.04	5.69	6.15	6.03
Supplemental:							
Obsidian	PHM	6.9[d]	7.28	8.18	7.47	7.64	10.72
Obsidian	LGB	4.1[d]	3.98	3.83	4.13	3.98	-2.93
Obsidian	LVC	--	5.82	6.42	6.10	6.11	--
Additional:							
Granite	PPG	< 100[e]	5.63	6.98	--	6.31	--
Basalt	BCR-1	1.75[b]	1.84	2.35	1.95	2.05	17.14
Basalt	BHVO-1	0.42[b]	0.388	0.618	0.502	0.503	19.76
Soil	SRM-2709	3[b, f]	2.81	3.58	3.18	3.19	6.33
Soil	GSD-5	2.6[b, g]	2.52	3.15	2.79	2.82	8.46
Soil	SJS	< 100[e]	3.30	4.14	3.79	3.74	--

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] NIST Certificate of Analysis for SRM-2709 (1993).

[g] Xie, Yan, Li and Shen (1985).

Table B-27. Vanadium (V) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	9[a]	8.69	8.54	8.23	8.49	-5.67
Rhyolite Obsidian	RGM-1	13[a, b]	13.5	13.6	14.1	13.7	5.38
Supplemental:							
Obsidian	PHM	--	5.79	6.53	6.46	6.26	--
Obsidian	LGB	--	5.31	4.02	4.11	4.48	--
Obsidian	LVC	--	6.76	6.03	7.34	6.71	--
Additional:							
Granite	PPG	35[c]	39.6	42.7	--	41.2	17.71
Basalt	BCR-1	407[a]	425	427	505	452	11.06
Basalt	BHVO-1	317[a, d]	309	342	294	315	-0.63
Soil	SRM-2709	112[a, e]	106	111	117	111	-0.89
Soil	GSD-5	109[a, f]	106	106	109	107	-1.83
Soil	SJS	130[c]	125	131	141	132	1.54

[a] Govindaraju (1994).

[b] USGS Certificate of Analysis for RGM-1 (1995).

[c] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[d] USGS Certificate of Analysis for BHVO-1 (1995).

[e] NIST Certificate of Analysis for SRM-2709 (1993).

[f] Xie, Yan, Li and Shen (1985).

Table B-28. Tungsten (W) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	--	2.20	2.10	2.15	2.15	--
Rhyolite Obsidian	RGM-1	1.5 [a, b]	1.70	1.55	1.30	1.52	1.33
Supplemental:							
Obsidian	PHM	--	1.10	1.03	0.950	1.03	--
Obsidian	LGB	--	1.15	0.850	0.850	0.950	--
Obsidian	LVC	--	2.60	2.55	2.65	2.60	--
Additional:							
Granite	PPG	--	0.900	0.900	--	0.900	--
Basalt	BCR-1	0.44 [b]	0.500	0.500	0.400	0.467	6.14
Basalt	BHVO-1	0.27 [b, c]	0.200	0.300	0.250	0.250	-7.41
Soil	SRM-2709	2 [b, d]	1.90	2.10	1.95	1.98	-1.00
Soil	GSD-5	3.2 [b, e]	3.20	3.15	2.85	3.07	-4.06
Soil	SJS	--	2.10	2.05	2.10	2.08	--

[a] USGS Certificate of Analysis for RGM-1 (1995).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for BHVO-1 (1995).

[d] NIST Certificate of Analysis for SRM-2709 (1993).

[e] Xie, Yan, Li and Shen (1985).

Table B-29. Yttrium (Y) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	39 [a]	41.3	38.3	41.2	40.3	3.33
Rhyolite Obsidian	RGM-1	25 [a, b]	23.5	25.5	23.5	24.2	-3.20
Supplemental:							
Obsidian	PHM	--	122	119	113	118	--
Obsidian	LGB	--	24.7	25.5	25.5	25.2	--
Obsidian	LVC	--	15.4	16.2	16.4	16.0	--
Additional:							
Granite	PPG	95 [c]	105	102	--	104	9.47
Basalt	BCR-1	38 [a]	36.5	39.1	36.8	37.5	-1.32
Basalt	BHVO-1	27.6 [a, d]	25.1	29.8	26.0	27.0	-2.17
Soil	SRM-2709	18 [a, e]	16.2	17.4	16.7	16.8	-6.67
Soil	GSD-5	26 [a, f]	18.6	20.0	19.6	19.4	-25.38
Soil	SJS	16 [c]	16.2	18.3	17.6	17.4	8.75

[a] Govindaraju (1994).

[b] USGS Certificate of Analysis for RGM-1 (1995).

[c] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[d] USGS Certificate of Analysis for BHVO-1 (1995).

[e] NIST Certificate of Analysis for SRM-2709 (1993).

[f] Xie, Yan, Li and Shen (1985).

Table B-30. Zinc (Zn) Values for Laboratory Standards Used in This Project.

All values reported in ppm.

Standard Type and Composition	Standard	Accepted Value	Run 1 Value	Run 2 Value	Run 3 Value	Mean Value	Percent Difference
Critical:							
Obsidian	SRM-278	55 [a, b]	51.0	50.8	51.8	51.2	-6.91
Rhyolite Obsidian	RGM-1	32 [b, c]	34.3	34.6	33.8	34.2	6.88
Supplemental:							
Obsidian	PHM	191 [d]	239	265	236	247	29.32
Obsidian	LGB	31 [d]	38.5	39.4	47.3	41.7	34.52
Obsidian	LVC	--	58.2	63.2	66.9	62.8	--
Additional:							
Granite	PPG	110 [e]	125	119	--	122	10.91
Basalt	BCR-1	129.5 [b]	135	130	129	131	1.16
Basalt	BHVO-1	105 [b, f]	92.6	103	93.4	96.3	-8.29
Soil	SRM-2709	106 [b, g]	114	108	102	108	1.89
Soil	GSD-5	243 [b, h]	270	265	259	265	9.05
Soil	SJS	110 [e]	135	119	124	126	14.55

[a] NIST Certificate of Analysis for SRM-278 (1992).

[b] Govindaraju (1994).

[c] USGS Certificate of Analysis for RGM-1 (1995).

[d] Glascock (1999).

[e] "Accepted Values for [USGS] In-House Standards" (undated), received from Dr. James Crock, USGS, on 4/27/99.

[f] USGS Certificate of Analysis for BHVO-1 (1995).

[g] NIST Certificate of Analysis for SRM-2709 (1993).

[h] Xie, Yan, Li and Shen (1985).

APPENDIX C
ARTIFACT SAMPLES

This Appendix presents descriptive information about the 100 artifacts of unknown composition studied in this project, which consisted of 96 pieces of obsidian, 2 pieces of other lithic materials, and 2 shards of pottery. Although, as discussed in Chapter 3, all 96 pieces of obsidian and both pieces of other lithic materials fall under the category of "debitage," a catch-all term used by archaeologists to signify unwanted or unusable pieces or chips left over from the manufacture of blades, points, scrapers, and other tools (Frederick Lange, verbal communication November 1999), they are artifacts in the most general sense of the term, having been produced by man. Please see Figures C-1 through C-10 for photographs; other, close-up photographs are in possession of the author of this study. The information presented in this Appendix includes: 1) the chemical analyses obtained via ICP-MS for all 100 artifacts, and, 2) certain external and internal characteristics of all 100 artifacts, as observed visually.

Chemical Analysis of the Artifacts

All 100 artifacts included in this study were analyzed via ICP-MS to determine their chemical compositions, and this data is presented (to 3 significant digits) in Table C-1. This data is presented as "rock concentrations" in ppm; the compositional data has been "back calculated" into element concentrations within the solid artifacts, just as if they had been measured in that form. If interested, the reader may refer to Briggs and Meier (1999) for the mechanics of this calculation. As discussed in Appendix B, Repeat Measurements section, 19 obsidian debitage pieces were subjected to "repeated" measurements wherein the same digested aliquot was sampled by the instrument twice. Eight of the 19 (CS-01, CS-07, CS-11, VT-35, VT-36, VT-37, VT-38, and VT-42), were extremely low mass, thus their entire (or nearly so) mass was used in the single analytical sample, thus obtaining as much information as possible about them was extremely important; unfortunately, for 4 of these 8 (CS-07, VT-35, VT-36, and VT-42), the second measurements were deemed unusable. All chemical data presented in Table C-1

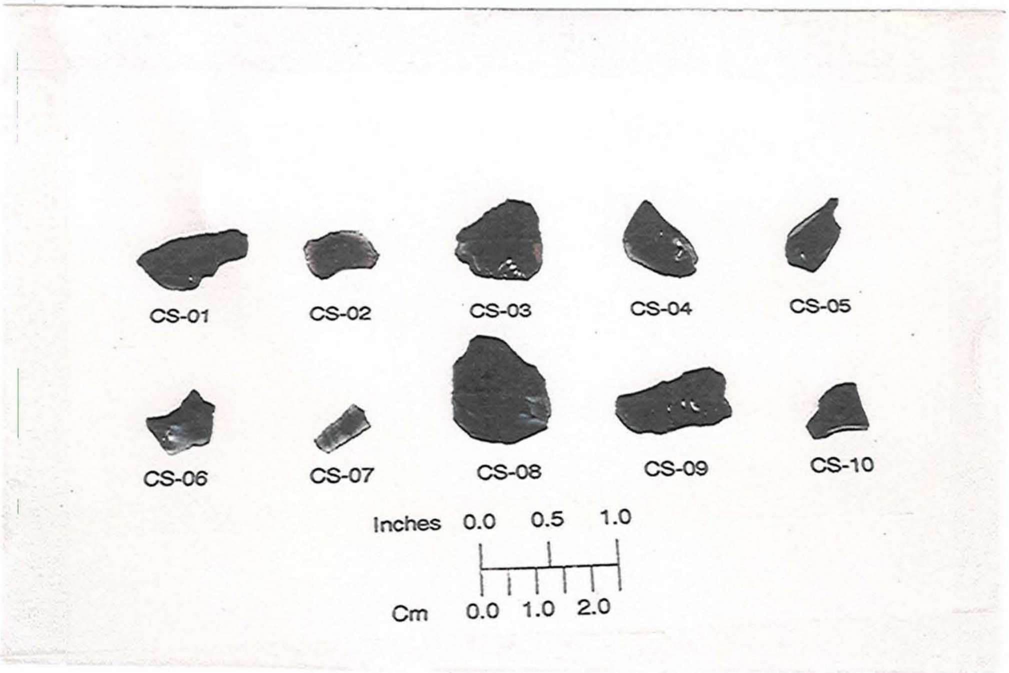


Figure C-1. Artifacts CS-01 through CS-10. Any white spots seen on the artifacts are due to camera flashback.

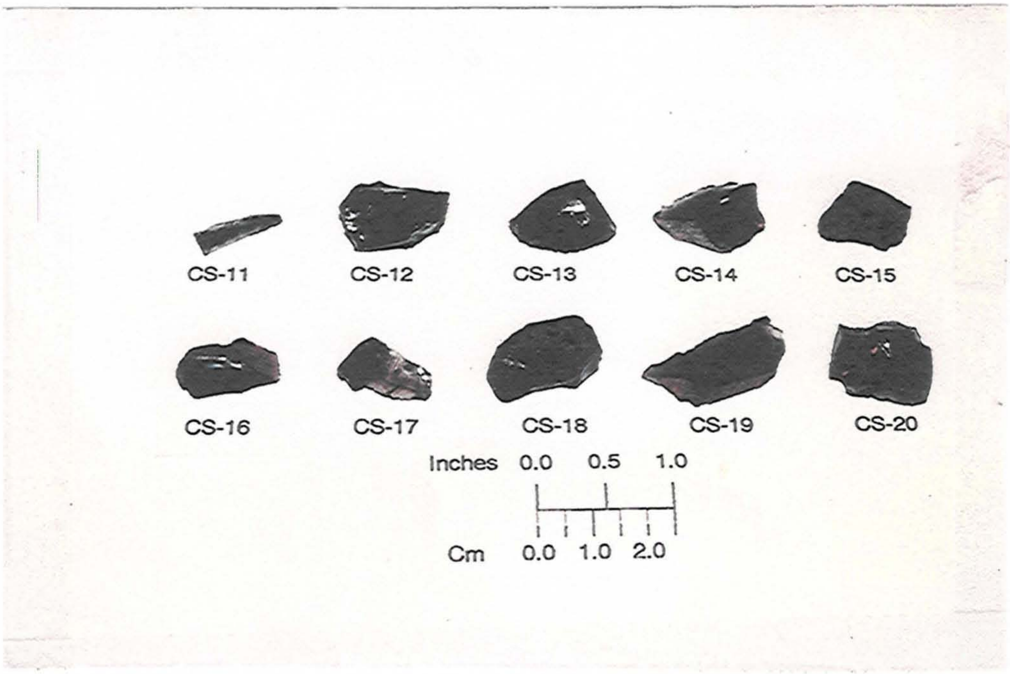


Figure C-2. Artifacts CS-11 through CS-20. Any white spots seen on the artifacts are due to camera flashback.

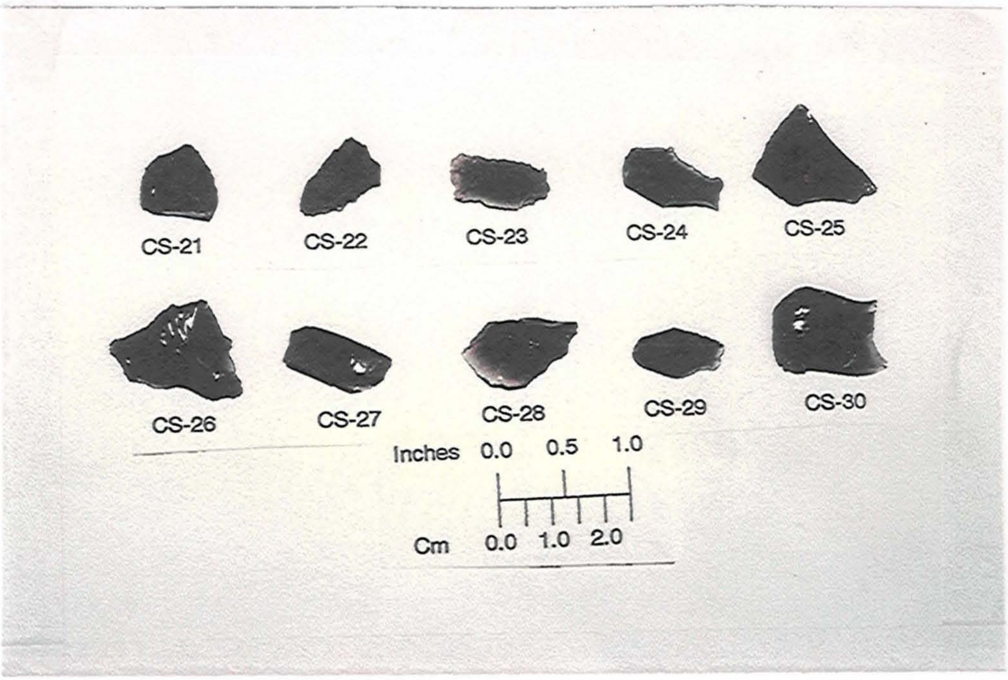


Figure C-3. Artifacts CS-21 through CS-30. Any white spots seen on the artifacts are due to camera flashback.

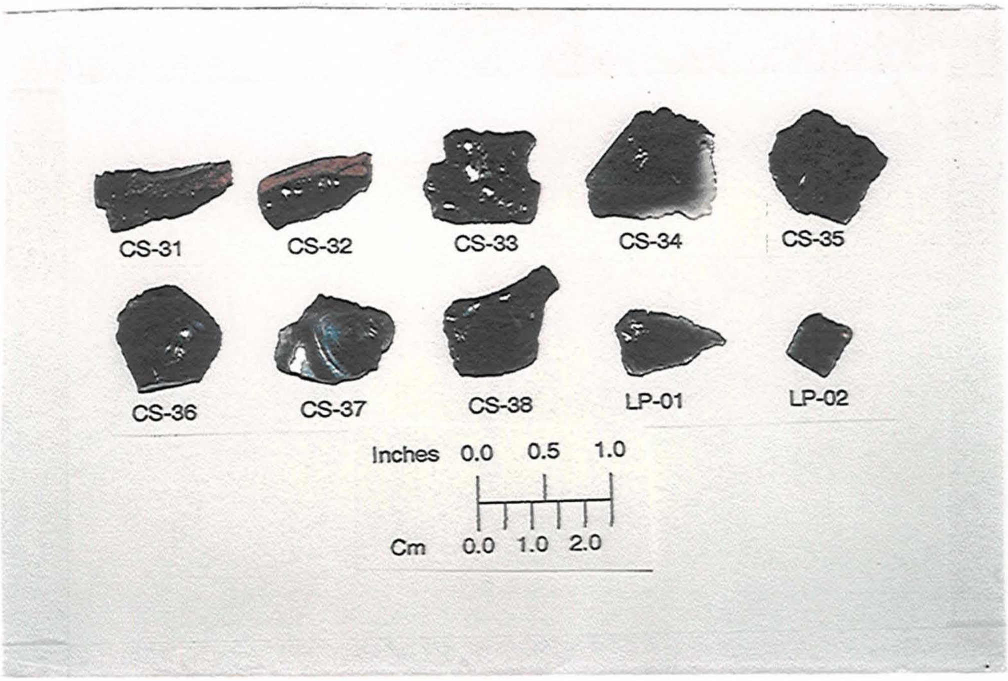


Figure C-4. Artifacts CS-31 through CS-38, and LP-01 through LP-02. Any white spots seen on the artifacts are due to camera flashback.

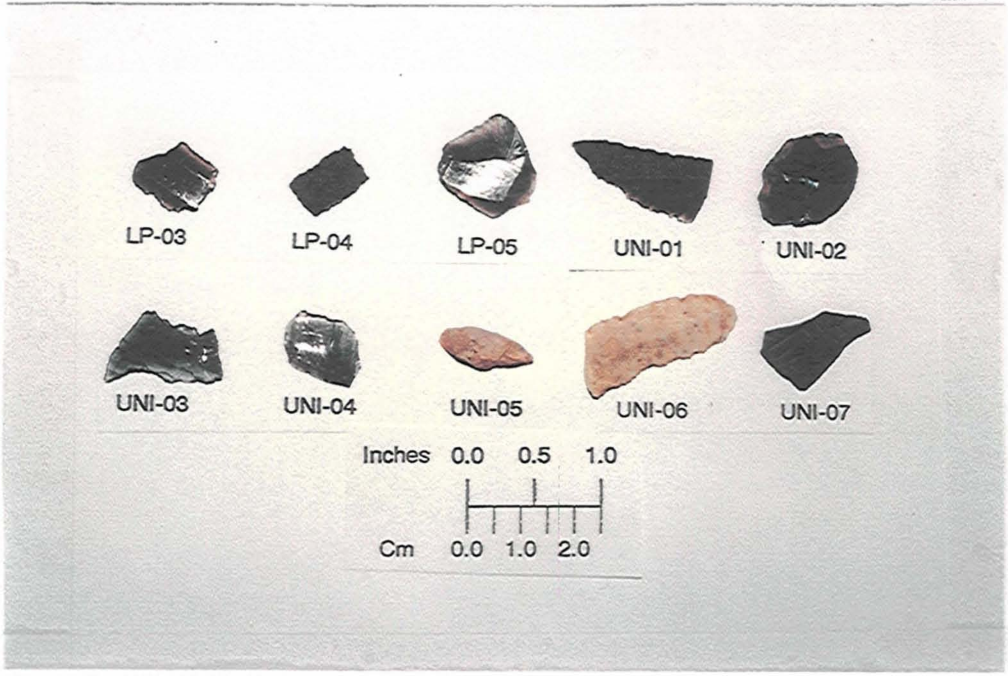


Figure C-5. Artifacts LP-03 through LP-05, and UNI-01 through UNI-07. Any white spots seen on the artifacts are due to camera flashback.

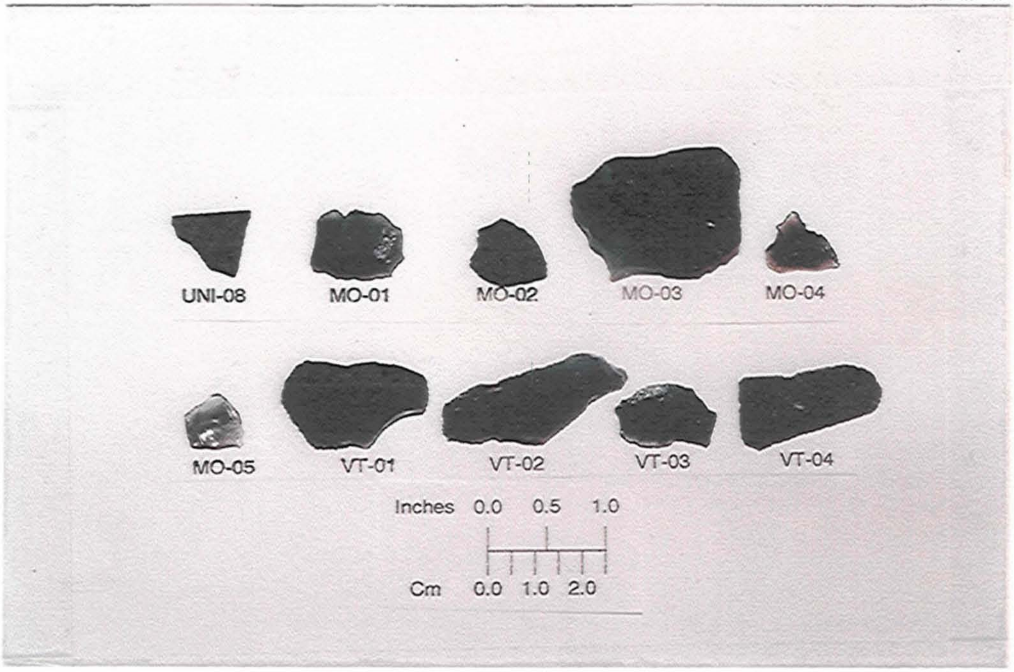


Figure C-6. Artifacts UNI-08, MO-01 through MO-05, and VT-01 through VT-04. All white spots are due to camera flashback, except those on right side of artifact MO-01 and top left of artifact VT-03, which are remnants of labeling material.

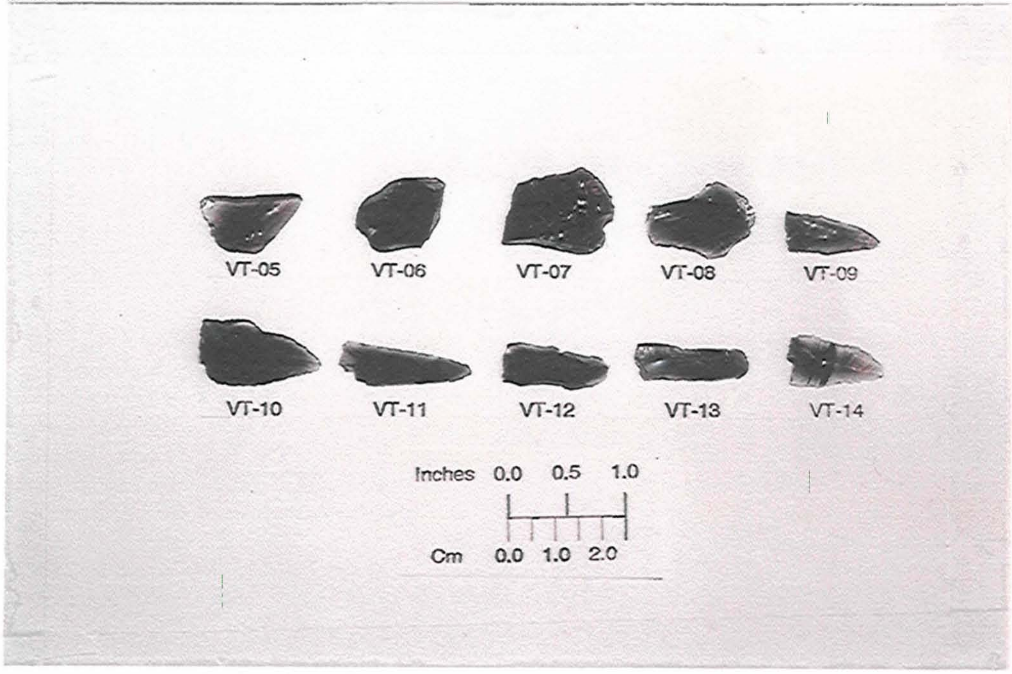


Figure C-7. Artifacts VT-05 through VT-14. Any white spots seen on the artifacts are due to camera flashback.

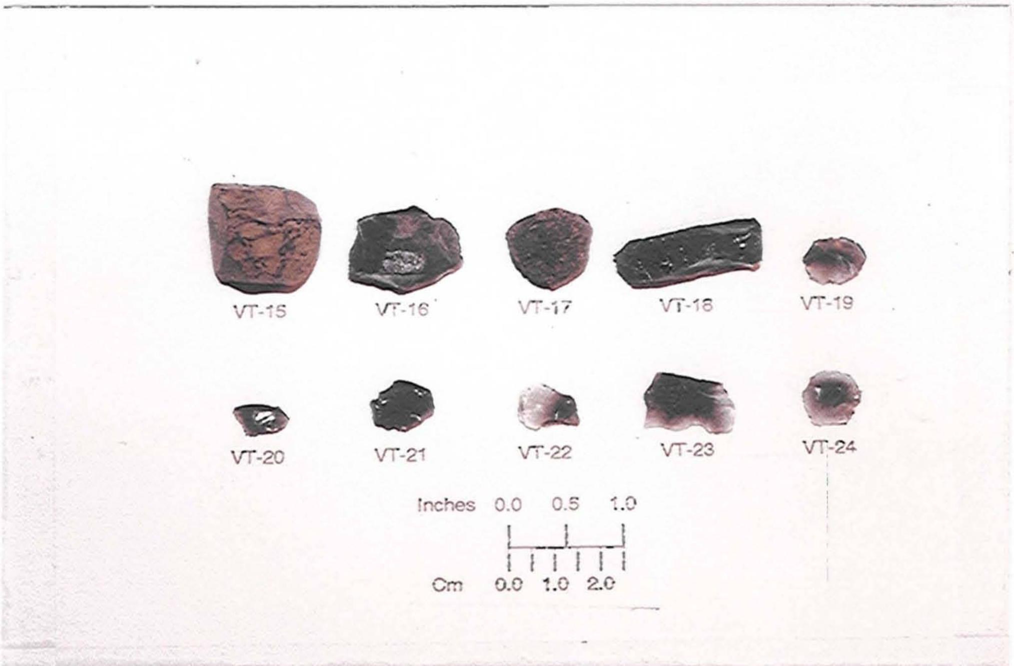


Figure C-8. Artifacts VT-15 through VT-24. All white spots seen on the artifacts are due to camera flashback, except in lower center of artifact VT-16, which is remnant of labeling material.

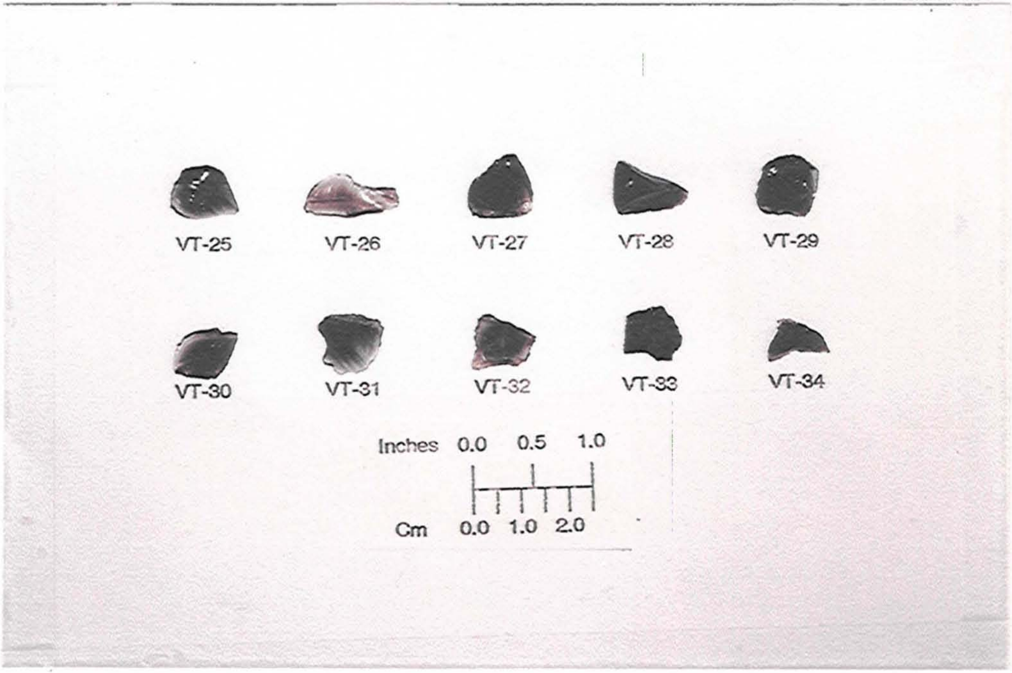


Figure C-9. Artifacts VT-25 through VT-34. Any white spots seen on the artifacts are due to camera flashback.

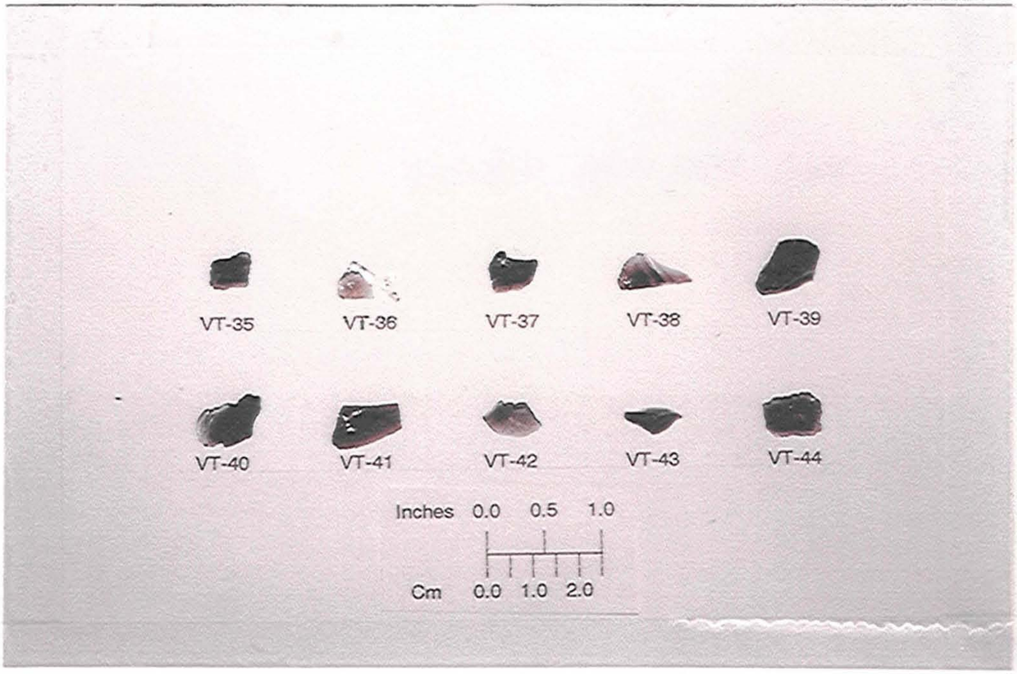


Figure C-10. Artifacts VT-35 through VT-44. Any white spots seen on the artifacts are due to camera flashback.

Table C-1. Analytical Results (in ppm) for Artifact Samples Studied in This Project, as Determined by ICP-MS.

Obsidian Artifact Samples

Sample ID	Aluminum (Al) Value	Barium (Ba) Value	Calcium (Ca) Value	Cerium (Ce) Value	Chromium (Cr) Value	Cesium (Cs) Value	Copper (Cu) Value
CS-01	75300	995	8850	52.4	13.5	7.63	37.6
CS-02	64700	846	6400	51.0	357	4.73	*< 3*
CS-03	65800	1090	6980	51.9	401	8.37	*< 3*
CS-04	64700	1090	6890	52.8	769	8.77	*< 3*
CS-05	66900	1000	6890	51.0	959	8.27	*< 3*
CS-06	87800	979	9020	53.8	21.1	7.81	73.5
CS-07	61300	1000	6110	47.4	4.46	7.98	11.8
CS-08	61900	1050	6600	49.7	167	8.27	152
CS-09	63600	1090	6980	52.8	234	8.77	23.6
CS-10	61300	1000	6500	47.4	323	8.37	*< 3*
CS-11	60800	887	6210	45.6	9.48	7.29	*< 3*
CS-12	68800	929	8300	49.1	257	7.37	9.90
CS-13	60200	1090	6400	47.4	201	8.37	201
CS-14	*> 70000*	1110	9700	58.0	368	8.59	40.6
CS-15	61900	1000	6600	50.1	245	8.08	61.4
CS-16	63600	1000	6690	50.1	335	8.37	*< 3*
CS-17	60200	1000	6500	50.1	290	8.27	43.7
CS-18	63600	1050	6790	50.6	212	8.37	23.6
CS-19	55800	910	5530	47.4	223	7.78	*< 3*
CS-20	61300	1090	6210	51.9	223	8.27	51.9
CS-21	62400	1000	6400	51.0	190	8.18	59.0
CS-22	58000	1000	6010	48.3	201	8.08	61.4
CS-23	63600	1090	6690	51.9	4.46	8.67	49.6
CS-24	63600	1000	6500	51.0	234	8.27	35.4
CS-25	63600	1050	6600	51.5	134	8.32	23.6
CS-26	*> 70000*	1110	9600	55.8	282	8.28	19.8
CS-27	62400	1090	6600	53.7	8.92	8.47	35.4
CS-28	65800	1090	6790	51.0	190	8.27	42.5
CS-29	62400	1090	6400	51.9	19.0	8.27	107
CS-30	64700	1090	6790	51.9	234	8.47	23.6
CS-31	85500	890	8640	50.6	293	7.63	114
CS-32	69100	1090	7180	53.7	368	8.77	56.6
CS-33	64700	1000	6690	53.7	190	8.08	74.3
CS-34	62400	1090	6600	53.7	167	8.37	23.6
CS-35	56900	1000	6210	48.3	178	7.78	10.6
CS-36	92300	1070	9600	55.9	398	8.56	10.4

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Aluminum (Al) Value	Barium (Ba) Value	Calcium (Ca) Value	Cerium (Ce) Value	Chromium (Cr) Value	Cesium (Cs) Value	Copper (Cu) Value
CS-37	31200	537	2910	26.0	93.7	4.53	*< 3*
CS-38	71000	929	8300	49.1	282	7.37	9.90
LP-01	62400	1000	6790	49.7	987	8.18	23.6
LP-02	64700	1000	7180	50.1	4.46	8.18	4.72
LP-03	75300	1010	8900	45.7	7.35	2.73	218
LP-04	64700	1000	6890	50.1	2.23	8.08	*< 3*
LP-05	86600	979	8640	46.4	281	2.70	6.21
UNI-01	66700	960	8200	39.0	355	2.42	40.6
UNI-02	84400	890	8830	50.6	328	7.63	31.1
UNI-03	86600	979	8930	53.8	328	7.91	47.6
UNI-04	73100	819	7870	43.3	3.51	6.70	20.7
MO-01	87800	1070	9600	54.9	304	8.56	10.4
MO-02	83800	979	9070	54.9	316	7.91	6.73
MO-03	73100	1010	9000	53.0	343	7.83	76.2
MO-04	85500	979	9020	44.3	328	2.60	20.7
MO-05	81000	979	8740	52.8	4.68	7.81	32.1
VT-01	78200	979	9020	49.6	281	7.77	83.8
VT-02	73100	1010	8800	50.7	374	7.73	63.9
VT-03	85500	979	9120	54.9	246	7.91	10.4
VT-04	71000	939	8400	49.1	343	7.47	30.7
VT-05	84400	979	8640	49.6	281	7.63	31.1
VT-06	74300	872	8540	42.2	281	7.63	8.28
VT-07	76500	890	8640	47.5	351	7.63	8.28
VT-08	81000	979	8830	48.5	246	7.91	9.32
VT-09	84400	979	8830	49.6	7.02	7.91	20.7
VT-10	80400	979	9070	50.1	333	7.67	10.4
VT-11	90000	979	9020	54.9	7.02	7.72	20.7
VT-12	85500	979	9500	50.6	281	8.18	7.25
VT-13	75400	979	8830	48.5	293	7.63	9.32
VT-14	79900	979	9020	48.5	5.85	7.81	20.7
VT-15	73100	1110	10000	56.3	361	8.43	41.6
VT-16	75900	979	9070	49.1	357	7.86	15.5
VT-17	*> 70000*	1110	10000	59.1	539	8.89	19.8
VT-18	74200	960	8600	51.3	319	7.47	19.8
VT-19	81000	979	8640	46.4	5.85	7.63	61.1
VT-20	78800	979	8930	50.6	5.85	7.81	31.1
VT-21	81000	1070	9410	51.7	328	8.00	20.7
VT-22	78800	979	8830	49.6	8.19	7.53	10.4

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Aluminum (Al) Value	Barium (Ba) Value	Calcium (Ca) Value	Cerium (Ce) Value	Chromium (Cr) Value	Cesium (Cs) Value	Copper (Cu) Value
VT-23	75400	979	9120	48.0	298	7.72	6.21
VT-24	81000	979	8830	50.6	18.7	7.63	135
VT-25	76500	979	9120	51.7	11.7	7.72	8.28
VT-26	67700	970	8400	46.8	4.90	7.37	19.8
VT-27	68800	970	8400	46.8	233	7.37	5.94
VT-28	75300	960	8500	52.4	270	7.47	9.90
VT-29	73100	960	8600	50.2	355	7.58	5.94
VT-30	75300	1010	8600	53.5	7.35	7.58	19.8
VT-31	74200	990	8850	53.5	14.1	7.78	73.3
VT-32	*> 70000*	1110	9500	53.5	7.35	7.98	19.8
VT-33	*> 70000*	980	8700	52.4	306	7.58	35.6
VT-34	*> 70000*	1010	9200	54.6	15.9	7.88	59.4
VT-35	*> 70000*	1010	9000	53.5	13.5	7.68	63.4
VT-36	*> 70000*	1010	9000	52.4	4.90	7.68	*< 3*
VT-37	67200	960	8300	43.5	15.9	7.37	85.6
VT-38	75300	1060	9050	54.6	29.4	7.98	62.9
VT-39	*> 70000*	1210	10000	55.8	441	8.79	9.90
VT-40	76300	1010	8900	51.3	14.7	7.68	52.5
VT-41	76300	1010	8950	52.4	17.2	7.78	19.8
VT-42	*> 70000*	1110	9500	56.9	4.90	7.98	3.96
VT-43	*> 70000*	1110	9400	55.8	12.3	8.08	109
VT-44	*> 70000*	1010	9000	52.4	18.4	7.68	57.4

Non-Obsidian Artifact Samples *

Sample Number	Aluminum (Al) Value	Barium (Ba) Value	Calcium (Ca) Value	Cerium (Ce) Value	Chromium (Cr) Value	Cesium (Cs) Value	Copper (Cu) Value
UNI-05	1720	253	*< 500*	0.446	1150	*< 0.1*	119
UNI-06	968	24.2	*< 500*	6.02	1350	*< 0.1*	93.1
UNI-07	*> 90000*	1250	17300	24.3	16.4	1.12	145
UNI-08	*> 90000*	1250	11500	21.1	33.9	0.930	186

* UNI-05 is a quartz pebble, UNI-06 is a blade of silicified conglomerate, and both UNI-07 and UNI-08 are pottery shards.

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Iron (Fe) Value	Gallium (Ga) Value	Potassium (K) Value	Lanthanum (La) Value	Lithium (Li) Value	Magnesium (Mg) Value	Manganese (Mn) Value
CS-01	7640	12.0	37200	30.2	65.6	699	473
CS-02	10100	12.0	34600	30.2	45.2	990	397
CS-03	11100	11.0	33500	31.0	64.1	660	481
CS-04	10100	11.0	33500	31.8	60.9	660	533
CS-05	11100	11.0	32400	29.5	65.1	660	575
CS-06	9290	12.3	39100	31.0	65.5	868	554
CS-07	7170	10.1	31300	28.7	59.9	550	428
CS-08	8430	10.1	31300	29.8	59.9	550	455
CS-09	8480	11.0	33500	30.2	62.0	660	460
CS-10	9190	11.0	32400	27.9	66.2	550	449
CS-11	7520	9.66	30200	27.5	60.9	550	428
CS-12	8020	12.0	34200	27.1	61.5	699	444
CS-13	8180	10.1	31300	28.7	59.9	550	428
CS-14	11500	14.0	42200	33.2	70.7	816	529
CS-15	8890	10.1	31900	30.2	60.9	605	455
CS-16	9490	11.0	32400	30.2	63.0	550	470
CS-17	8590	10.1	31300	30.2	62.0	550	439
CS-18	9140	10.6	32400	30.6	63.5	605	470
CS-19	7580	9.02	28100	27.9	52.5	550	387
CS-20	8080	10.1	30200	30.2	58.8	550	418
CS-21	8690	10.1	32400	31.0	65.1	550	449
CS-22	7980	10.1	30200	29.5	55.7	550	408
CS-23	7270	11.0	32400	31.8	58.8	550	439
CS-24	9090	11.0	31300	30.2	65.1	550	470
CS-25	8430	10.6	31900	30.6	59.9	605	455
CS-26	9450	14.0	40200	32.2	69.7	816	510
CS-27	7270	11.0	31300	31.8	59.9	660	439
CS-28	8890	11.0	33500	31.0	63.0	550	470
CS-29	7170	10.1	31300	31.0	57.8	550	428
CS-30	8890	11.0	32400	31.8	62.0	660	460
CS-31	10100	12.3	37300	29.1	61.9	868	533
CS-32	10100	11.0	33500	31.8	65.1	660	491
CS-33	9090	10.1	31300	31.8	63.0	660	481
CS-34	8480	10.1	31300	31.8	59.9	550	449
CS-35	8380	10.1	30200	29.5	56.7	550	428
CS-36	12100	13.2	41900	32.9	70.1	992	596

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Iron (Fe) Value	Gallium (Ga) Value	Potassium (K) Value	Lanthanum (La) Value	Lithium (Li) Value	Magnesium (Mg) Value	Manganese (Mn) Value
CS-37	4550	5.24	16200	15.5	30.5	220	219
CS-38	8400	12.0	35200	28.1	61.5	699	454
LP-01	13600	11.0	32400	30.2	59.9	550	496
LP-02	8280	11.0	32400	29.5	62.0	550	481
LP-03	7830	14.0	37200	25.1	35.9	1510	416
LP-04	7980	11.0	32400	29.5	60.9	660	470
LP-05	12100	12.3	37300	26.3	35.5	1860	490
UNI-01	9170	12.0	34200	22.1	31.8	1630	387
UNI-02	11100	12.3	37300	28.2	64.6	868	533
UNI-03	11100	12.3	38200	31.0	65.5	992	564
UNI-04	8080	10.6	34600	25.4	59.2	744	469
MO-01	11100	13.2	41000	32.0	71.0	992	586
MO-02	11100	12.8	38700	31.5	68.3	868	586
MO-03	9550	13.0	38200	30.7	66.6	757	501
MO-04	12100	12.3	37300	25.4	34.6	2730	479
MO-05	8790	12.3	38200	30.1	63.7	868	533
VT-01	11100	12.8	38700	30.6	66.4	806	538
VT-02	11500	13.0	38700	28.1	66.1	699	482
VT-03	11100	13.2	39100	31.0	67.3	868	564
VT-04	8790	12.0	36200	28.1	63.6	699	454
VT-05	10100	12.3	39100	29.1	65.5	868	543
VT-06	11100	12.3	38200	26.3	64.6	744	522
VT-07	11100	12.3	38200	28.2	63.7	868	533
VT-08	11100	12.3	39100	29.1	67.3	868	554
VT-09	9190	12.3	38200	28.2	65.5	868	554
VT-10	11100	12.8	39100	30.1	66.4	868	554
VT-11	9190	12.3	40000	31.0	68.3	992	564
VT-12	11100	13.2	41900	30.1	67.3	868	564
VT-13	11100	12.3	38200	29.1	63.7	744	533
VT-14	9190	13.2	39100	29.1	65.5	868	543
VT-15	11500	13.5	41700	32.7	70.7	816	539
VT-16	11100	12.8	39600	31.0	66.4	868	538
VT-17	15300	15.0	42200	34.2	74.8	816	567
VT-18	9070	12.0	36200	29.1	64.6	699	473
VT-19	9090	12.3	38200	28.2	66.4	868	533
VT-20	8990	12.3	38200	30.1	65.5	868	533
VT-21	11100	13.2	41900	32.0	67.3	868	554
VT-22	9090	12.3	38200	30.1	64.6	868	533

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Iron (Fe) Value	Gallium (Ga) Value	Potassium (K) Value	Lanthanum (La) Value	Lithium (Li) Value	Magnesium (Mg) Value	Manganese (Mn) Value
VT-23	11100	13.2	40000	30.6	61.0	868	533
VT-24	9190	12.3	39100	31.0	66.4	868	543
VT-25	9190	13.2	39100	31.0	67.3	868	533
VT-26	7350	12.0	36200	27.1	61.5	699	454
VT-27	8400	12.0	36200	28.1	62.5	699	463
VT-28	8880	12.0	36200	30.2	63.6	699	482
VT-29	9070	13.0	37200	29.1	64.6	699	473
VT-30	7540	12.0	37200	30.2	65.6	699	473
VT-31	8120	12.5	38700	30.7	67.7	757	491
VT-32	8310	14.0	40200	31.2	69.7	816	510
VT-33	9260	13.0	37200	30.2	68.7	699	491
VT-34	8310	13.0	39200	32.2	68.7	816	510
VT-35	8210	13.0	38200	31.2	65.6	699	501
VT-36	8210	13.0	38200	30.2	65.6	816	406
VT-37	7930	12.0	35700	26.1	59.5	699	454
VT-38	8450	13.0	38700	31.7	66.6	757	501
VT-39	11500	15.0	43200	34.2	74.8	816	558
VT-40	7930	12.0	38200	29.1	65.6	699	482
VT-41	8310	12.5	39200	31.2	65.6	757	487
VT-42	8790	13.0	40200	33.2	69.7	816	529
VT-43	8600	14.0	40200	33.2	66.6	816	529
VT-44	8310	13.0	38200	31.2	66.6	699	491

Non-Obsidian Artifact Samples, continued *

Sample Number	Iron (Fe) Value	Gallium (Ga) Value	Potassium (K) Value	Lanthanum (La) Value	Lithium (Li) Value	Magnesium (Mg) Value	Manganese (Mn) Value
UNI-05	6400	0.800	503	0.201	14.4	< *100*	37.8
UNI-06	7260	3.70	402	5.13	6.25	< *100*	33.1
UNI-07	68700	15.8	10900	11.3	10.9	12400	948
UNI-08	83800	20.2	4730	7.80	8.19	8560	746

* UNI-05 is a quartz pebble, UNI-06 is a blade of silicified conglomerate, and both UNI-07 and UNI-08 are pottery shards.

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Sodium (Na) Value	Niobium (Nb) Value	Nickel (Ni) Value	Lead (Pb) Value	Rubidium (Rb) Value	Strontium (Sr) Value	Tantalum (Ta) Value
CS-01	27100	11.7	5.05	19.4	159	178	1.15
CS-02	25400	12.2	9.31	15.6	144	158	1.13
CS-03	24400	11.3	14.7	19.3	174	189	1.23
CS-04	24400	7.90	9.51	19.3	154	189	0.945
CS-05	24400	8.18	9.31	18.4	154	189	0.945
CS-06	29000	10.6	9.60	19.5	166	185	1.05
CS-07	22300	7.05	2.06	17.5	144	158	0.756
CS-08	23300	7.94	8.28	17.9	154	184	0.898
CS-09	24400	8.27	6.27	19.3	164	189	1.04
CS-10	23300	8.46	7.74	18.4	144	179	1.04
CS-11	22300	7.38	4.36	17.0	144	168	0.803
CS-12	24700	8.58	9.80	17.2	148	165	0.864
CS-13	23300	7.90	6.17	18.4	144	168	1.04
CS-14	28500	10.1	13.1	20.4	170	203	1.06
CS-15	23300	9.31	9.02	18.9	149	179	1.09
CS-16	23300	7.90	8.04	18.4	154	189	0.851
CS-17	23300	7.71	7.35	18.4	154	179	0.851
CS-18	23900	8.41	10.2	18.9	154	184	0.945
CS-19	20300	7.05	4.41	17.5	133	147	0.851
CS-20	22300	8.46	7.25	18.4	144	168	1.04
CS-21	23300	8.08	7.45	18.4	154	168	0.851
CS-22	22300	8.27	6.27	18.4	144	158	1.13
CS-23	23300	11.3	2.55	19.3	154	168	1.23
CS-24	23300	8.46	8.43	18.4	154	168	0.851
CS-25	23300	7.85	4.36	18.4	154	179	0.898
CS-26	28500	10.1	7.98	19.4	170	191	0.960
CS-27	22300	7.90	4.12	19.3	154	179	0.945
CS-28	24400	7.90	5.88	18.4	154	189	0.851
CS-29	22300	7.61	8.92	18.4	154	168	0.945
CS-30	24400	8.65	7.94	19.3	154	168	1.04
CS-31	28000	9.41	13.9	18.5	156	175	1.05
CS-32	25400	11.3	10.8	21.2	164	200	1.13
CS-33	23300	7.99	5.39	18.4	154	168	0.851
CS-34	23300	8.27	5.29	18.4	144	168	1.04
CS-35	21300	7.80	6.47	17.5	144	168	0.945
CS-36	31800	9.60	12.9	20.5	176	185	1.05

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Sodium (Na) Value	Niobium (Nb) Value	Nickel (Ni) Value	Lead (Pb) Value	Rubidium (Rb) Value	Strontium (Sr) Value	Tantalum (Ta) Value
CS-37	12200	4.14	2.25	10.1	76.9	91.4	0.473
CS-38	25700	8.58	6.77	17.2	148	178	0.864
LP-01	23300	9.17	25.5	18.4	154	173	0.945
LP-02	24400	8.27	2.35	18.4	154	168	0.851
LP-03	31400	13.3	2.32	15.1	97.6	165	1.06
LP-04	24400	7.99	1.18	18.4	154	179	0.851
LP-05	33800	11.5	8.32	16.6	97.5	155	0.836
UNI-01	28500	9.36	8.48	14.0	88.5	140	0.768
UNI-02	28000	9.12	7.82	18.5	156	175	1.05
UNI-03	29000	9.60	7.52	19.5	166	185	1.05
UNI-04	26100	7.97	1.68	16.6	137	155	0.836
MO-01	30900	9.60	5.74	20.5	176	196	1.15
MO-02	28000	9.07	11.4	19.5	166	191	1.05
MO-03	27600	9.36	15.7	18.3	159	184	1.06
MO-04	32800	9.60	11.9	15.6	97.5	155	0.836
MO-05	28000	9.02	1.78	19.5	156	185	1.05
VT-01	28500	8.35	15.3	18.0	161	175	0.993
VT-02	27100	10.1	10.6	19.4	153	178	1.15
VT-03	29000	9.22	9.90	19.5	166	185	1.05
VT-04	24700	8.58	9.70	17.2	148	178	0.864
VT-05	29000	8.64	9.90	18.5	156	175	1.05
VT-06	29900	8.93	9.50	18.5	146	155	1.05
VT-07	29000	8.74	10.9	17.6	156	165	1.05
VT-08	30900	8.64	9.21	17.6	166	175	0.941
VT-09	29900	9.12	3.56	18.5	156	175	1.05
VT-10	29000	8.83	10.9	18.5	166	180	1.05
VT-11	29900	9.02	3.17	19.5	166	185	1.05
VT-12	30900	9.12	8.12	20.5	176	185	1.05
VT-13	28000	8.45	6.53	18.5	156	175	0.941
VT-14	29000	9.02	2.97	19.5	166	185	1.05
VT-15	29500	10.1	15.2	22.0	170	216	1.15
VT-16	29000	8.83	16.3	17.6	166	180	0.993
VT-17	29500	10.1	13.1	21.5	182	203	1.06
VT-18	26600	8.58	9.60	18.3	159	178	0.960
VT-19	29900	8.16	2.67	17.6	166	175	0.941
VT-20	29000	8.35	2.67	17.6	166	185	0.941
VT-21	29900	9.50	9.80	17.6	176	185	1.15
VT-22	29000	8.16	3.76	18.5	156	175	0.941

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Sodium (Na) Value	Niobium (Nb) Value	Nickel (Ni) Value	Lead (Pb) Value	Rubidium (Rb) Value	Strontium (Sr) Value	Tantalum (Ta) Value
VT-23	28500	12.5	6.53	17.1	166	180	1.36
VT-24	29000	8.64	8.71	18.5	156	175	1.05
VT-25	28000	8.54	4.75	18.5	166	175	1.05
VT-26	25700	9.36	1.92	17.2	148	165	0.960
VT-27	25700	7.80	4.95	17.2	148	165	0.864
VT-28	25700	10.9	11.1	18.3	159	178	1.25
VT-29	26600	8.58	11.1	18.3	148	178	0.960
VT-30	26600	9.36	2.42	18.3	159	178	0.960
VT-31	27100	8.97	5.40	18.8	153	178	1.01
VT-32	28500	9.36	2.02	19.4	170	191	1.06
VT-33	27600	9.36	13.1	18.3	159	178	1.06
VT-34	28500	9.36	6.26	19.4	159	178	1.06
VT-35	27600	9.36	4.65	19.4	159	178	0.960
VT-36	27600	9.36	0.606	19.4	159	178	0.960
VT-37	26600	8.58	6.41	17.7	136	159	1.01
VT-38	28000	9.75	12.6	19.9	159	184	1.06
VT-39	30400	9.36	10.1	20.4	170	203	1.06
VT-40	27600	8.58	5.25	18.3	159	178	0.960
VT-41	28000	8.58	6.57	18.8	159	178	1.01
VT-42	28500	9.36	1.01	20.4	159	191	1.06
VT-43	28500	9.36	4.44	19.4	159	191	1.06
VT-44	27600	8.58	7.47	19.4	159	178	0.960

Non-Obsidian Artifact Samples, continued *

Sample Number	Sodium (Na) Value	Niobium (Nb) Value	Nickel (Ni) Value	Lead (Pb) Value	Rubidium (Rb) Value	Strontium (Sr) Value	Tantalum (Ta) Value
UNI-05	380	0.312	31.3	0.215	1.36	5.72	*< 0.1*
UNI-06	190	1.09	30.3	1.94	0.908	25.4	*< 0.1*
UNI-07	7330	6.53	10.9	6.14	37.1	247	0.627
UNI-08	2510	6.53	21.8	6.63	17.6	155	0.732

* UNI-05 is a quartz pebble, UNI-06 is a blade of silicified conglomerate, and both UNI-07 and UNI-08 are pottery shards.

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Thorium (Th) Value	Thallium (Tl) Value	Uranium (U) Value	Vanadium (V) Value	Tungsten (W) Value	Yttrium (Y) Value	Zinc (Zn) Value
CS-01	12.3	1.04	4.46	3.53	1.75	16.7	45.6
CS-02	11.7	0.840	3.98	7.72	1.10	14.6	33.3
CS-03	12.7	1.23	4.56	5.79	1.90	16.2	35.4
CS-04	13.7	1.23	4.75	8.69	1.90	16.2	35.4
CS-05	12.7	1.12	4.46	10.6	2.00	16.2	35.4
CS-06	13.6	1.07	5.43	3.02	1.80	17.0	51.8
CS-07	11.7	1.12	4.17	4.83	1.10	14.6	35.4
CS-08	12.2	1.18	4.32	4.83	1.70	15.4	55.6
CS-09	13.7	1.23	4.75	4.83	2.00	15.4	38.5
CS-10	12.7	1.23	4.27	4.83	1.70	14.6	32.2
CS-11	11.7	1.01	4.07	3.86	1.10	14.6	32.2
CS-12	12.3	1.10	4.24	3.53	1.60	15.7	37.1
CS-13	13.7	1.23	4.66	3.86	1.80	14.6	60.3
CS-14	13.4	1.34	4.91	4.70	1.80	18.6	48.4
CS-15	12.7	1.12	4.61	4.83	1.75	15.4	41.1
CS-16	12.7	1.12	4.37	5.79	1.60	15.4	34.3
CS-17	12.7	1.12	4.46	4.83	1.70	15.4	39.5
CS-18	12.7	1.18	4.46	5.31	1.60	15.4	37.4
CS-19	11.7	1.12	4.37	3.86	1.60	13.8	31.2
CS-20	12.7	1.12	4.75	3.86	1.70	14.6	39.5
CS-21	12.7	1.12	4.46	3.86	1.50	15.4	41.6
CS-22	12.7	1.12	4.66	3.86	1.70	14.6	40.6
CS-23	13.7	1.12	5.04	3.86	1.80	15.4	41.6
CS-24	11.7	1.12	4.27	4.83	1.60	15.4	63.4
CS-25	12.7	1.18	4.66	3.86	2.45	15.8	38.0
CS-26	13.4	1.34	4.79	4.70	1.70	18.6	42.8
CS-27	13.7	1.23	4.75	3.86	1.70	15.4	37.4
CS-28	12.7	1.23	4.37	4.83	1.50	16.2	39.5
CS-29	12.7	1.12	4.75	3.86	1.60	15.4	47.8
CS-30	12.7	1.23	4.75	4.83	1.70	15.4	37.4
CS-31	12.5	1.07	4.82	4.02	1.80	16.2	58.3
CS-32	13.7	1.34	5.04	4.83	1.80	16.2	43.7
CS-33	11.7	1.12	4.66	4.83	1.40	16.2	45.8
CS-34	12.7	1.12	4.95	4.83	1.70	15.4	37.4
CS-35	11.7	1.01	4.27	4.83	1.60	14.6	32.2
CS-36	13.6	1.17	5.19	5.03	1.90	17.9	42.1

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Thorium (Th) Value	Thallium (Tl) Value	Uranium (U) Value	Vanadium (V) Value	Tungsten (W) Value	Yttrium (Y) Value	Zinc (Zn) Value
CS-37	7.02	0.560	2.43	2.90	0.800	7.86	20.8
CS-38	12.3	1.10	4.24	3.53	1.60	15.7	37.1
LP-01	12.2	1.12	4.51	7.72	1.80	15.4	38.0
LP-02	12.7	1.12	4.37	4.83	1.40	16.2	35.4
LP-03	7.36	0.610	2.34	9.40	1.00	16.7	72.0
LP-04	12.7	1.12	4.46	4.83	1.70	15.4	35.4
LP-05	8.15	0.746	2.96	9.05	1.20	17.0	32.4
UNI-01	6.80	0.610	2.23	10.6	0.900	14.7	36.0
UNI-02	13.6	0.959	5.06	4.02	1.90	17.0	42.1
UNI-03	12.5	1.28	5.19	4.02	1.90	17.0	47.5
UNI-04	11.5	0.959	3.58	3.02	1.50	14.5	38.9
MO-01	14.6	1.28	5.06	4.02	2.00	17.9	43.2
MO-02	13.6	1.07	5.50	4.02	1.90	17.4	39.4
MO-03	12.8	1.16	4.52	4.70	1.75	16.7	51.8
MO-04	7.73	0.639	2.72	10.1	1.00	16.2	37.8
MO-05	14.6	1.07	5.06	3.02	1.70	17.0	44.3
VT-01	13.1	1.17	4.26	4.02	1.80	17.0	51.3
VT-02	12.3	1.22	4.35	9.40	1.85	16.2	49.5
VT-03	13.6	1.07	5.31	4.02	1.90	17.0	41.0
VT-04	12.3	1.10	4.13	3.53	1.60	15.7	40.5
VT-05	12.5	1.07	4.82	4.02	1.80	17.0	49.7
VT-06	11.5	1.28	3.46	4.02	1.90	14.5	38.9
VT-07	12.5	1.07	3.83	4.02	1.90	16.2	37.8
VT-08	12.5	1.17	4.08	4.02	1.80	17.0	40.0
VT-09	12.5	0.959	4.08	3.02	1.70	16.2	42.1
VT-10	13.1	1.12	4.57	4.02	1.80	17.0	39.4
VT-11	13.6	1.07	5.19	3.02	1.70	17.0	41.0
VT-12	13.6	1.17	4.57	4.02	1.90	17.0	41.0
VT-13	12.5	1.17	4.45	4.02	1.80	16.2	40.0
VT-14	13.6	1.07	4.32	3.02	1.80	17.0	43.2
VT-15	13.9	1.28	4.79	4.70	1.95	18.1	48.4
VT-16	13.6	1.12	4.26	4.52	1.75	17.0	41.0
VT-17	14.5	1.34	5.24	10.6	1.90	19.6	45.0
VT-18	12.3	1.22	4.46	3.53	1.60	15.7	40.5
VT-19	12.5	1.17	3.95	3.02	1.60	17.0	47.5
VT-20	12.5	1.07	3.95	3.02	1.60	17.0	44.3
VT-21	13.6	1.17	4.32	5.03	1.80	18.7	41.0
VT-22	13.6	1.07	4.32	4.02	1.60	17.0	40.0

Table C-1 (continued). Analytical Results (in ppm) for Artifact Samples.

Obsidian Artifact Samples, continued

Sample ID	Thorium (Th) Value	Thallium (Tl) Value	Uranium (U) Value	Vanadium (V) Value	Tungsten (W) Value	Yttrium (Y) Value	Zinc (Zn) Value
VT-23	13.6	1.07	4.01	4.52	1.70	17.0	38.9
VT-24	12.5	1.07	4.20	4.02	1.70	17.0	60.5
VT-25	13.6	1.07	4.45	4.02	1.60	17.0	38.9
VT-26	11.2	0.976	3.68	2.35	1.40	15.7	38.3
VT-27	11.2	0.976	3.68	3.53	1.50	15.7	36.0
VT-28	13.4	1.10	4.68	3.53	1.80	16.7	37.1
VT-29	12.3	1.10	4.35	3.53	1.70	16.7	38.3
VT-30	12.3	1.10	4.68	2.35	1.60	16.7	38.3
VT-31	12.8	1.10	4.52	2.94	1.65	16.2	50.6
VT-32	13.4	1.10	4.35	3.53	1.70	17.6	42.8
VT-33	12.3	1.22	4.68	4.70	2.00	16.7	42.8
VT-34	13.4	1.10	4.79	3.53	1.70	17.6	48.4
VT-35	13.4	1.10	4.68	2.35	1.50	16.7	47.3
VT-36	12.3	1.10	4.91	2.35	1.20	16.7	36.0
VT-37	11.2	1.04	3.51	3.53	1.60	14.7	51.2
VT-38	13.4	1.22	4.79	3.53	1.75	17.2	48.4
VT-39	14.5	1.34	4.91	5.88	1.90	18.6	42.8
VT-40	12.3	1.10	4.35	3.53	1.50	16.7	45.0
VT-41	12.8	1.16	4.57	3.53	1.55	16.7	40.5
VT-42	13.4	1.10	5.13	3.53	1.40	17.6	39.4
VT-43	13.4	1.22	4.91	3.53	1.80	17.6	59.6
VT-44	12.3	1.22	4.46	3.53	1.50	16.7	48.4

Non-Obsidian Artifact Samples, continued *

Sample Number	Thorium (Th) Value	Thallium (Tl) Value	Uranium (U) Value	Vanadium (V) Value	Tungsten (W) Value	Yttrium (Y) Value	Zinc (Zn) Value
UNI-05	*< 0.05*	*< 0.1*	0.335	8.23	0.300	0.294	22.5
UNI-06	0.847	*< 0.1*	0.223	15.3	0.400	0.784	22.5
UNI-07	2.61	0.213	1.24	513	1.60	23.0	89.6
UNI-08	2.72	0.213	1.24	251	1.10	19.6	78.8

* UNI-05 is a quartz pebble, UNI-06 is a blade of silicified conglomerate, and both UNI-07 and UNI-08 are pottery shards.

for 15 obsidian debitage pieces (CS-01, CS-02, CS-06, CS-07, CS-11, CS-15, CS-25, LP-01, MO-02, VT-02, VT-10, VT-23, VT-31, VT-35, VT-36, VT-37, VT-38, VT-41, and VT-42) are the arithmetic means (averages) of 2 measurements.

As detailed in Appendix A, ICP-MS Methodology section, the instrument used was housed at the USGS, Denver Federal Center, Lakewood, USA, and operated by Allen Meier, Research Chemist with the Crustal Imaging and Characterization Team, Geological Division, USGS. Appendix A includes information regarding how the raw instrument response data is interpreted into compositional information, and Table A-2 lists the lower limits of detection for the instrument used. The reader is referred to such excellent texts as Jarvis et al. (1992), Johnstone and Rose (1996), Taylor (2001), and Watson (1997), for other ICP-MS information.

Artifact Descriptions

One hundred artifacts were studied here: 96 obsidian pieces, 2 pieces of other lithic materials, and 2 pottery shards. All 96 obsidian artifacts and both other lithic artifacts fall under the category of "debitage," a catch-all term used by archaeologists to signify unwanted or unusable pieces and chips left over from the manufacture of blades, points, scrapers, and other tools (Frederick Lange, verbal communication November 1999), while the 2 pottery shards are just that, broken pieces ("shards" or "sherds") of pottery. Basic summarized physical information is given below, with further details presented in Table C-2 (presented at the end of this Appendix), including some internal details for the 96 obsidian artifacts. The reader is referred to the Geological Society of America Rock Color Chart (1995) for explanation of the Munsell color system and determination of colors and color names. Certain characteristics are not addressed here, particularly those that are more archaeologically-oriented, such as type and style of tool, style of manufacture, extent of wear, amount and/or type of use prior to discard, etc.; such characteristics, their analysis and possible implications, are beyond the scope of this study. Some of these data can be found in Lange (1995 ed., 1996 ed.), and other data are intended for future publication (Frederick Lange, verbal communication November 1999). However, brief comments are made below regarding surface wear on both non-obsidian lithic debitage pieces as observed here.

Obsidian Artifacts

The 96 obsidian pieces were of various sizes, shapes and masses, had a small range of colors, and had varying amounts of surface wear, "working" (by knapping or chipping), and weathered surfaces. Please refer to Figures C-1 through C-10 for photographs of these pieces, and Table C-2 (at the end of this Appendix) for further information. The size and mass of the obsidian debitage pieces ranged from the extremely small VT-36 (~1 x 1 x 0.1 cm, 0.0821 g), the smallest pieces, to the fairly large MO-03 (~3.5 x 3 x 3.5 cm, 17.9730 g), the largest. The shape of the majority of obsidian pieces ranged from irregular chunks (for example: CS-08, MO-03, VT-15), to irregular chips (for example: CS-06, CS-10, VT-05), although 2 appeared to be broken portions of arrowheads (CS-33 and MO-01), and possibly as many as 16 appeared to be broken portions of prismatic (elongate) blades (CS-07, CS-11, CS-22, CS-31, CS-32, LP-02, LP-03, LP-04, UNI-01, VT-09, VT-10, VT-11, VT-12, VT-13, VT-14, and VT-44). The color of the obsidian represented by these pieces did not vary greatly, ranging from the darkest, "black," the Munsell "N1" designation (for example: CS-03, UNI-02, VT-03), to the lightest, "grayish black," N2 (for example: CS-07, LP-03, VT-14) (GSA 1995). As described in more detail in Appendix A, Sample Cleaning section, the labeling materials placed on the artifacts were somewhat difficult to remove, especially from those with irregular surfaces. Small portions of the white backgrounds of the labels could not be removed from 3 obsidian pieces: MO-01, right side of artifact (Figure C-6), VT-03, top left (Figure C-6), and VT-16, lower center (Figure C-8).

All 96 obsidian debitage pieces were observed to have "worked" and/or "unworked" surfaces, as termed here. "Worked" surfaces were nearly always vitreous, and consisted of knapped or chipped surfaces, the conchoidally-fractured surfaces resulting from the deliberate chipping away of material by man to reveal fresh obsidian, or being unwanted material that had been chipped off other pieces. The amount of worked surfaces on the obsidian pieces ranged from 0% (just 1 piece, VT-15), to 100% (30 pieces; for example: CS-02, UNI-01, and VT-20), although the majority of pieces (65 pieces; for example: CS-01, LP-01, and VT-17) had some amount in-between. The "unworked" surfaces were dullish, with irregular contours ranging from somewhat polyhedral (for example: CS-03, CS-19, CS-32, and VT-15), to somewhat vesicular (for example: CS-23, CS-31, MO-01, VT-01, and VT-04), although many surfaces appeared to be simply somewhat uneven or irregular (for example: CS-05, CS-18, LP-01, MO-03, and VT-16). These unworked surfaces on the obsidian pieces are likely remnants of the original cooling "crusts" that had formed on the outermost surfaces of the obsidian flows, when the hot lava met the cooler air (or water) and cooled very rapidly (see Chapter 2). None of the worked surfaces showed more than light weathering, with the most highly-weathered pieces (only 3; listed in order of increasing surface dullness: LP-05, CS-06, UNI-01) being only somewhat dull, most likely the result of contact with water and/or moisture, and the various chemical constituents carried by such, over a period of time (see Chapter 2). A number of unworked surfaces appeared to show a low to moderate degree of weathering (for example: CS-03, CS-32, MO-03, VT-15); cooling "crusts" can also weather over time, as they come into contact with water and/or moisture.

There were 2 other surfaces, each different, and upon first observation appeared to be the result of weathering, although closer observations revealed they were much more likely to be different forms of cooling "crusts." The first, observed only on piece CS-14, consisted of a whitish to brownish, silvery to pearly "coating," making up the single, smallish, unworked surface on that piece. Close examination (at 40x magnification), revealed that this "coating" consisted of very tiny (~<0.1 mm), rounded gas bubbles trapped just below the surface of the obsidian. During the rapid cooling that takes place at the surface of an extruded hot magma (lava) as it contacts the much cooler air, gas within the magma comes out of solution very quickly (see for example: Best 2003; Hall 1996; Wilson 1989). It is quite likely that such gasses, trapped on their way out of the solidifying lava, are the source of these tiny trapped gas bubbles seen just under the surface of this piece. The second type, also observed on only 1 piece (VT-31), consisted of a grayish "coating," also making up the single, small, unworked surface on that piece. Close examination (also at 40x), revealed this "coating" to consist of tiny (~1 mm) angular bits of glass protruding from the surface, with no apparent orientation. If an extruded magma (lava) comes into contact with water, it will chill extremely quickly, essentially becoming "flash-cooled," and a broken or fragmented surface can result (see for example: Best 2003; Hall 1996; Wilson 1989); this was very likely the origin of this surface.

Other Lithic Artifacts

Two of the 4 non-obsidian artifacts were composed of other lithic materials, each different. Please refer to Figure C-5 for a photograph of these 2 debitage pieces, and Table C-2 for more information. These 2 pieces consisted of materials not of prime interest in this study, therefore less detailed descriptions are given here for them than for the obsidian pieces. The first of these, UNI-05, consisted of a small (~3.25 x 1.5 x 1.5 cm, 1.0046 g), opaque, teardrop-shaped, angular piece of massive quartz, which might more properly be called a quartz pebble. The color of this piece ranged from "very pale orange," 10 YR 8/2, to "pale grayish orange," 10 YR 8/4 (GSA 1995). There was some iron staining on this piece, whose color ranged from "dark yellowish orange," 10 YR 6/6, to "dusky yellowish brown," 10 YR 2/2 (GSA 1995). Although the quartz pebble did have some physical attributes that are suggestive of debitage, and it was referred to as a "punta de talador de cuarzo" ("quartz drill point") in the archaeological site excavation report (Bargnesi et al. 1996:Figure 3.5), it may more likely be a naturally-shaped piece, as no wear was observed on the piece by this researcher (at up to 40x magnification). However, quartz is a harder material than obsidian, and wear, if it had occurred on the piece, might not be observable until a higher magnification.

The second of these 2 pieces, UNI-06, consisted of a moderately-sized (~7 x 3 x 0.35 cm, 1.5441 g), broken portion of a thin, prismatic (elongate) blade composed of opaque, silicified conglomerate. The overall color of the piece was "pale grayish orange," 10 YR 7.5/3 (GSA 1995). The piece consisted of matrix-supported conglomeratic fragments (xenoliths) of various sizes, ranging from subangular to rounded in shape. The xenoliths had somewhat unclear boundaries, suggesting they may have been partially resorbed (Blatt 1992; Carozzi 1993). The largest xenolith was roughly 1 cm x 1 cm in size, while the smallest xenoliths were <1 mm in size. The matrix material comprises roughly 50% of the artifact by volume, and is "very pale yellowish brown," 10 YR 7/2 (GSA 1995). The lighter-colored xenoliths ranged from "yellowish gray" (5 Y 8/1) and "very pale orange" (10 YR 8/2), to "pale grayish orange" (10 YR 8/4) (GSA 1995). The darker-colored xenoliths ranged from "dark yellowish orange" (10 YR 6/6) to "moderate yellowish brown" (10 YR 5/4) (GSA 1995). There was some iron staining on this piece also, whose color ranged from "moderate brown" (5 YR 4/4) and "moderate yellowish brown" (5 YR 3/4), to "dark yellowish brown" (10 YR 4/2) (GSA 1995). Overall, some wear was observed on the edges of this piece (at up to 40x magnification), suggesting that it had been used prior to being discarded. The entire surface of this artifact had a matte-like, dullish appearance and feel which might be interpreted as the result of light to moderate weathering.

Pottery Shards

The last 2 artifacts consisted of opaque, unglazed, wedge-shaped pottery shards that were porous, of a light density, each a different color and having different design(s) incised or impressed into just one surface. Please refer to Figures C-5 and C-6 for photographs of these 2 artifacts, and Table C-2 for more information. These 2 artifacts also consisted of materials not of primary interest here, and fewer details are presented for these as well. The first (UNI-07) was moderately-sized (~4 x 2.5 x 0.25 cm, 0.7860 g), and "moderate grayish brown" in color, 5 YR 3/3 (GSA 1995). The mineral grains comprising this pottery ranged up to the lower end of the coarse sand size range (~0.5 mm; Jackson 1997). The surface into which a design had been incised or impressed was convex in shape, thus likely an outer surface (Anderson 1985; Rice 1987). Although much of the ground-in soil on the surface of this shard had been removed during cleaning (see Appendix A), a small amount still remained and could not be removed without also removing pottery material, as it was fairly soft and easily scratched. Due to the softness of this piece, it is most likely of unfired pottery, or possibly fired, though at quite a low temperature (Anderson 1985; Rice 1987). The second pottery shard (artifact UNI-08) was moderately-sized (~4 x 3.75 x 0.25 cm, 0.4556 g), and "grayish black" in color, N2.5 (GSA 1995). The mineral grains comprising this pottery ranged up to the lower end of the medium sand size range (~0.25 mm; Jackson 1997). The surface into which a design had been incised or impressed was concave in shape, thus likely an inner surface (Anderson 1985; Rice 1987). This shard had also been coated with soil, although its surfaces were much harder than those of the first shard, thus allowing for nearly all of the soil to be removed during the cleaning process. This harder quality is indicative of fired pottery (Anderson 1985; Rice 1987).

Table C-2. Artifact Descriptions.

Sample # (this Author's label)	**Field #** (archaeologist's label)	**Flat #** (flat on which artifact was taped)	**Position on Flat** (position on the flat)	**Piece #** (piece #'s, if artifact was broken up)	**Content of Piece** (what the piece consists of)	**Thin Section #**	**Content of Thin Section**	**Initial Weight (g)**	**Weight of Powder (g)**
CS-01	1-309	1-CS	not noted	whole piece	obsidian	--	--	1.2443	n/a
"	"	"	"	1	~1/2 artifact, w/ Cu drops	--	--	n/a	n/a
"	"	"	"	"	"	A	large Cu drop	"	"
"	"	"	"	"	"	B	small Cu drop	"	"
"	"	"	"	2	~1/2 artifact, w/ no Cu drops	--	--	0.2486	0.2270
CS-02	1-309	1-CS	not noted	whole piece	obsidian	--	--	0.4553	0.4422
CS-03	1-313	1-CS	not noted	whole piece	obsidian	--	--	1.4409	1.3360
CS-04	1-314	1-CS	not noted	whole piece	obsidian	--	--	1.0182	0.9797
CS-05	1-314	1-CS	not noted	whole piece	obsidian	--	--	0.6886	0.6627
CS-06	1-314	1-CS	not noted	whole piece	obsidian	--	--	0.4750	0.4399
CS-07	1-318	1-CS	not noted	whole piece	obsidian	--	--	0.1190	0.1068
CS-08	1-319	1-CS	not noted	whole piece	obsidian	--	--	4.7287	4.6606
CS-09	1-319	1-CS	not noted	whole piece	obsidian	--	--	1.3545	1.3215
CS-10	1-319	1-CS	not noted	whole piece	obsidian	--	--	0.7054	0.5923
CS-11	1-319	1-CS	not noted	whole piece	obsidian	--	--	0.1521	0.1392
CS-12	1-320	1-CS	not noted	whole piece	whole obsidian artifact	--	--	2.8180	n/a
"	"	"	"	"	~1/2 artifact, w/ no Cu drops	--	--	1.8322	1.7623
CS-13	1-320	1-CS	not noted	whole piece	obsidian	--	--	2.3355	2.3130
CS-14	1-320	1-CS	not noted	whole piece	obsidian	--	--	1.6800	1.6260
CS-15	1-320	1-CS	not noted	whole piece	obsidian	--	--	1.1241	1.1013
CS-16	1-320	1-CS	not noted	whole piece	obsidian	--	--	1.1166	1.0885
CS-17	1-320	1-CS	not noted	whole piece	obsidian	--	--	0.6958	0.6519
CS-18	1-321	1-CS	not noted	whole piece	obsidian	--	--	3.0290	2.9516
CS-19	1-321	1-CS	not noted	whole piece	obsidian	--	--	2.1138	2.0702
CS-20	1-321	1-CS	not noted	whole piece	obsidian	--	--	1.6847	1.6350
CS-21	1-321	1-CS	not noted	whole piece	obsidian	--	--	1.9190	1.8513
CS-22	1-321	1-CS	not noted	whole piece	obsidian	--	--	0.9638	0.9340
CS-23	1-321	1-CS	not noted	1	whole obsidian artifact	--	--	0.8650	n/a
"	"	"	"	2	~1/2 artifact, w/ no Cu drops	--	--	0.5180	0.4993

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**Field #** (archaeologist's label)	**Flat #** (flat on which artifact was taped)	**Position on Flat** (position on the flat)	**Piece #** (piece #'s, if artifact was broken up)	**Content of Piece** (what the piece consists of)	**Thin Section #**	**Content of Thin Section**	**Initial Weight (g)**	**Weight of Powder (g)**
CS-24	1-321	1-CS	not noted	whole piece	obsidian	--	--	0.9358	0.8996
CS-25	1-322	1-CS	not noted	whole piece	obsidian	--	--	1.9759	1.9286
CS-26	1-322	1-CS	not noted	1	whole obsidian artifact	--	--	1.5945	n/a
"	"	"		2	~1/2 artifact, w/ no Cu drops	--	--	0.8604	0.8002
CS-27	1-322	1-CS	not noted	1	whole obsidian artifact	--	--	1.3492	n/a
"	"	"	"	2	~1/2 artifact, w/ no Cu drops	--	--	0.4518	0.4376
CS-28	1-322	1-CS	not noted	whole piece	obsidian	--	--	1.2699	1.2214
CS-29	1-322	1-CS	not noted	whole piece	obsidian	--	--	0.5218	0.4950
CS-30	1-323	1-CS	not noted	whole piece	obsidian	--	--	2.2051	2.6549
CS-31	2-314(A)	2	A	whole piece	obsidian	--	--	1.4195	1.3625
CS-32	2-313(B)	2	B	whole piece	obsidian	--	--	1.1291	1.0939
CS-33	2-322(C)	2	C	whole piece	obsidian	--	--	1.7627	1.7131
CS-34	2-323(D)	2	D	whole piece	obsidian	--	--	2.5578	2.4758
CS-35	2-318(E)	2	E	whole piece	obsidian	--	--	2.0541	1.9910
CS-36	2-320(F)	2	F	whole piece	obsidian	--	--	2.2152	2.1641
CS-37	2-319(G)	2	G	whole piece	obsidian	--	--	1.2930	1.2654
CS-38	2-318(H)	2	H	whole piece	obsidian	--	--	1.5768	1.5162
LP-01	2-018?(A)	2	A	whole piece	obsidian	--	--	0.7952	0.7807
LP-02	2-00?(B)	2	B	whole piece	obsidian	--	--	0.3649	0.3504
LP-03	2-009(C)	2	C	whole piece	obsidian	--	--	0.6078	0.5748
LP-04	2-004(D)	2	D	whole piece	obsidian	--	--	0.4541	0.4350
LP-05	2-004?(E)	2	E	whole piece	obsidian	--	--	1.0950	1.0513
UNI-01	3-103(A)	3	A	whole piece	obsidian	--	--	1.0889	1.0436
UNI-02	3-126(B)	3	B	whole piece	obsidian	--	--	2.3644	2.3148
UNI-03	3-105(C)	3	C	whole piece	obsidian	--	--	0.7096	0.6832
UNI-04	3-103(D)	3	D	whole piece	obsidian	--	--	0.4200	0.4026
UNI-05	3-103(E)	3	E	whole piece	quartz pebble	--	--	1.0046	0.9466
"	"	"	"	"	"	--	--	"	"

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**Field #** (archaeologist's label)	**Flat #** (flat on which artifact was taped)	**Position on Flat** (position on the flat)	**Piece #** (piece #'s, if artifact was broken up)	**Content of Piece** (what the piece consists of)	**Thin Section #**	**Content of Thin Section**	**Initial Weight (g)**	**Weight of Powder (g)**
UNI-06	3-123(F)	3	F	whole piece	silicified conglomerate	--	--	1.5441	1.4859
"	"	"	"	"	"	--	--	"	"
"	"	"	"	"	"	--	--	"	"
"	"	"	"	"	"	--	--	"	"
"	"	"	"	"	"	--	--	"	"
UNI-07	3-008(G)	3	G	whole piece	pottery shard	--	--	0.7860	0.7436
UNI-08	3-132(H)	3	H	whole piece	pottery shard	--	--	0.4556	0.4226
MO-01	3-065(A)	3	A	whole piece	obsidian	--	--	1.4925	1.4592
MO-02	3-165(B)	3	B	whole piece	obsidian	--	--	2.3891	2.3369
MO-03	3-068(C)	3	C	whole piece	obsidian	--	--	17.9730	17.5454
MO-04	3-070(D)	3	D	whole piece	obsidian	--	--	0.6675	0.6373
MO-05	3-070(E)	3	E	whole piece	obsidian	--	--	0.3221	0.2995
VT-01	4-169(A)	4	A	whole piece	obsidian	--	--	4.6154	4.4451
VT-02	4-163(B)	4	B	whole piece	obsidian	--	--	4.2200	4.0066
VT-03	4-187(C)	4	C	whole piece	obsidian	--	--	1.5216	1.4869
VT-04	4-202(D)	4	D	whole piece	obsidian	--	--	1.4758	1.4160
VT-05	4-188(E)	4	E	whole piece	obsidian	--	--	0.8897	0.8533
VT-06	4-188(F)	4	F	whole piece	obsidian	--	--	1.8766	1.8249
VT-07	4-187(G)	4	G	whole piece	obsidian	--	--	2.9900	2.8895
VT-08	4-176(H)	4	H	whole piece	obsidian	--	--	1.5331	1.4915
VT-09	4-156(I)	4	I	whole piece	obsidian	--	--	0.5962	0.5083
VT-10	4-165(J)	4	J	whole piece	obsidian	--	--	2.1446	2.0659
VT-11	4-167(K)	4	K	whole piece	obsidian	--	--	0.8957	0.8546
VT-12	4-190(L)	4	L	whole piece	obsidian	--	--	0.9507	0.9044
VT-13	4-191(M)	4	M	whole piece	obsidian	--	--	0.7668	0.7291
VT-14	4-194(N)	4	N	whole piece	obsidian	--	--	0.5012	0.4734
VT-15	4-181(O)	4	O	whole piece	obsidian	--	--	13.5073	13.1844

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**Field #** (archaeologist's label)	**Flat #** (flat on which artifact was taped)	**Position on Flat** (position on the flat)	**Piece #** (piece #'s, if artifact was broken up)	**Content of Piece** (what the piece consists of)	**Thin Section #**	**Content of Thin Section**	**Initial Weight (g)**	**Weight of Powder (g)**
VT-16	4-065(P)	4	P	whole piece	obsidian	--	--	6.4100	6.2228
VT-17	4-191(Q)	4	Q	whole piece	obsidian	--	--	4.0021	3.8872
VT-18	4-187(R)	4	R	whole piece	obsidian	--	--	5.0959	4.9665
VT-19	5-188(A)	5	A	whole piece	obsidian	--	--	0.4342	0.4141
VT-20	5-188(B)	5	B	whole piece	obsidian	--	--	0.3000	0.2844
VT-21	5-188(C)	5	C	whole piece	obsidian	--	--	0.7518	0.7090
VT-22	5-188(D)	5	D	whole piece	obsidian	--	--	0.3107	0.2913
VT-23	5-188(E)	5	E	whole piece	obsidian	--	--	0.8233	0.7918
VT-24	5-188(F)	5	F	whole piece	obsidian	--	--	0.3052	0.2890
VT-25	5-188(G)	5	G	whole piece	obsidian	--	--	0.6291	0.6016
VT-26	5-188(H)	5	H	whole piece	obsidian	--	--	0.3820	0.3635
VT-27	5-188(I)	5	I	whole piece	obsidian	--	--	1.0152	0.9671
VT-28	5-188(J)	5	J	whole piece	obsidian	--	--	1.2945	1.2475
VT-29	5-188(K)	5	K	whole piece	obsidian	--	--	1.2217	1.1767
VT-30	5-188(L)	5	L	whole piece	obsidian	--	--	0.4780	0.4418
VT-31	5-188(M)	5	M	whole piece	obsidian	--	--	0.4384	0.4110
VT-32	5-188(N)	5	N	whole piece	obsidian	--	--	0.5262	0.4955
VT-33	5-188(O)	5	O	whole piece	obsidian	--	--	0.7352	0.6931
VT-34	5-188(P)	5	P	whole piece	obsidian	--	--	0.3742	0.3521
VT-35	5-188(Q)	5	Q	whole piece	obsidian	--	--	0.1771	0.1606
VT-36	5-188(R)	5	R	whole piece	obsidian	--	--	0.0821	0.0790
VT-37	5-188(S)	5	S	whole piece	obsidian	--	--	0.2149	0.1924
VT-38	5-188(T)	5	T	whole piece	obsidian	--	--	0.2247	0.2122
VT-39	5-188(U)	5	U	whole piece	obsidian	--	--	0.9675	0.9200
VT-40	5-188(V)	5	V	whole piece	obsidian	--	--	0.4869	0.4614
VT-41	5-188(W)	5	W	whole piece	obsidian	--	--	0.5212	0.4886
VT-42	5-188(X)	5	X	whole piece	obsidian	--	--	0.1484	0.1424
VT-43	5-188(Y)	5	Y	whole piece	obsidian	--	--	0.2800	0.2608
VT-44	5-188(Z)	5	Z	whole piece	obsidian	--	--	0.3406	0.3159

Geological Society of America. 1995. *GSA Rock Color Chart, with Genuine Munsell Color Chips*, 8th ed. 14 pages, including 6 plates of color chips.

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**"Surface" Color Designation** (using GSA Rock Color Chart 1995)	**"Surface" Color Name** (using GSA Rock Color Chart 1995)	**"Surface" Comments** (if applicable)
CS-01	N 1.5	Dark Grayish Black	--
"	"	"	--
"	"	"	--
"	"	"	--
"	"	"	--
CS-02	N 1.5	Dark Grayish Black	--
CS-03	N 1	Black	--
CS-04	N 1.5	Dark Grayish Black	--
CS-05	N 1.5	Dark Grayish Black	--
CS-06	N 1.5	Dark Grayish Black	--
CS-07	N 2	Grayish Black	--
CS-08	N 1.5	Dark Grayish Black	opaque
CS-09	N 2	Grayish Black	opaque
CS-10	N 1.5	Dark Grayish Black	opaque
CS-11	N 2	Grayish Black	--
CS-12	N 1	Black	opaque; "leached" surface
"	"	"	"
CS-13	N 1.5	Dark Grayish Black	--
CS-14	N 1.5	Dark Grayish Black	weathered surface "silvery" (tiny trapped gas bubbles)
CS-15	N 1.5	Dark Grayish Black	--
CS-16	N 1.5	Dark Grayish Black	opaque
CS-17	N 1.5	Dark Grayish Black	--
CS-18	N 1	Black	--
CS-19	N 1.5	Dark Grayish Black	--
CS-20	N 1.5	Dark Grayish Black	--
CS-21	N 2	Grayish Black	opaque
CS-22	N 1	Black	--
CS-23	N 2	Grayish Black	--
"	"	"	--

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	"Surface" Color Designation (using GSA Rock Color Chart 1995)	"Surface" Color Name (using GSA Rock Color Chart 1995)	"Surface" Comments (if applicable)
CS-24	N 1.5	Dark Grayish Black	opaque
CS-25	N 1	Black	--
CS-26	N 2	Grayish Black	opaque
"	"	"	--
CS-27	N 1.5	Dark Grayish Black	--
"	"	"	--
CS-28	N 1.5	Dark Grayish Black	--
CS-29	N 2	Grayish Black	--
CS-30	N 1.25	Very Dark Grayish Black	--
CS-31	N 1	Black	--
CS-32	N 1	Black	--
CS-33	N 1	Black	--
CS-34	N 1.5	Dark Grayish Black	--
CS-35	N 1	Black	opaque
CS-36	N 1.5	Dark Grayish Black	--
CS-37	N 1	Black	--
CS-38	N 1	Black	--
LP-01	N 1.5	Dark Grayish Black	--
LP-02	N 1.5	Dark Grayish Black	--
LP-03	N 2	Grayish Black	--
LP-04	N 2	Grayish Black	--
LP-05	N 2	Grayish Black	~50% of surface "leached"
UNI-01	N 2	Grayish Black	"leached" surface; opaque
UNI-02	N 1	Black	--
UNI-03	N 1.5	Dark Grayish Black	--
UNI-04	N 2	Grayish Black	--
UNI-05	10 YR 8/2 to 10 YR 8/4	Very Pale Orange to Pale Grayish Orange	opaque quartz pebble
"	10 YR 6/6 to 10 YR 2/2	Dark Yellowish Orange to Dusky Yellowish Brown	Fe staining on pebble

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**"Surface" Color Designation** (using GSA Rock Color Chart 1995)	**"Surface" Color Name** (using GSA Rock Color Chart 1995)	**"Surface" Comments** (if applicable)
UNI-06	10 YR 7.5/3	Pale Grayish Orange	opaque silicified conglomerate, overall color
"	10 YR 7/2	Very Pale Yellowish Brown	matrix; ~50% by volume
"	5 Y 8/1, 10 YR 8/2, 10 YR 8/4	Yellowish Gray, Very Pale Orange, Pale Grayish Orange	lighter-colored grains
"	10 YR 6/6, 10 YR 5/4	Dark Yellowish Orange, Moderate Yellowish Brown	darker-colored grains
"	5 YR 4/4, 5 YR 3/4, 10 YR 4/2	Mod. Brown, Mod. Yellowish Brown, Dark Yellowish Brown	Fe staining on artifact
UNI-07	5 YR 3/3	Moderate Grayish Brown	opaque pottery shard; soil encrusted
UNI-08	N 2.5	Grayish Black	opaque pottery shard
MO-01	N 1.5	Dark Grayish Black	semi-opaque
MO-02	N 2	Grayish Black	opaque
MO-03	N 1	Black	sort of "iridescent" coating over ~50%
MO-04	N 2	Grayish Black	--
MO-05	N 2	Grayish Black	--
VT-01	N 1	Black	opaque
VT-02	N 1	Black	--
VT-03	N 1	Black	--
VT-04	N 1.5	Dark Grayish Black	opaque
VT-05	N 2	Grayish Black	--
VT-06	N 1	Black	opaque
VT-07	N 1	Black	--
VT-08	N 2	Grayish Black	--
VT-09	N 2	Grayish Black	--
VT-10	N 2	Grayish Black	--
VT-11	N 2	Grayish Black	opaque
VT-12	N 2	Grayish Black	opaque
VT-13	N 2	Grayish Black	--
VT-14	N 2	Grayish Black	--
VT-15	N 1	Black	opaque

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**"Surface" Color Designation** (using GSA Rock Color Chart 1995)	**"Surface" Color Name** (using GSA Rock Color Chart 1995)	**"Surface" Comments** (if applicable)
VT-16	N 2	Grayish Black	opaque
VT-17	N 1	Black	--
VT-18	N 1	Black	--
VT-19	N 2	Grayish Black	opaque
VT-20	N 2	Grayish Black	--
VT-21	N 1	Black	--
VT-22	N 2	Grayish Black	--
VT-23	N 2	Grayish Black	--
VT-24	N 2	Grayish Black	--
VT-25	N 2	Grayish Black	--
VT-26	N 2	Grayish Black	--
VT-27	N 2	Grayish Black	--
VT-28	N 1	Black	--
VT-29	N 2	Grayish Black	--
VT-30	N 2	Grayish Black	--
VT-31	N 1.5	Dark Grayish Black	"crackly," broken weathering surface
VT-32	N 2	Grayish Black	--
VT-33	N 1	Black	--
VT-34	N 2	Grayish Black	opaque
VT-35	N 2	Grayish Black	opaque
VT-36	N 2	Grayish Black	--
VT-37	N 2	Grayish Black	--
VT-38	N 2	Grayish Black	--
VT-39	N 1	Black	opaque
VT-40	N 1.5	Dark Grayish Black	semi-opaque
VT-41	N 2	Grayish Black	semi-opaque
VT-42	N 2	Grayish Black	--
VT-43	N 1	Black	semi-opaque
VT-44	N 1	Black	--

Geological Society of America. 1995. *GSA Rock Color Chart, with Genuine Munsell Color Chips*, 8th ed. 14 pages, including 6 plates of color chips.

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**"Internal" Color Designation** (using GSA Rock Color Chart 1995)	**Color Name ("Internal")** (using GSA Rock Color Chart 1995)	**Presence of Copper Drops**	**Approximate Unworked Surface Area** (%)	**Presence of Microlites** (@ 40x)	**Presence of Banding** (@ 40x)	**Sample Shape**
CS-01	N 5	Medium Gray	Y	25	Y	Y	wedge-shaped
"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"
"	"	"	N	"	"	"	"
CS-02	N 6	Medium Light Gray	N	0	Y	Y	one side flat, other flaked
CS-03	N 5	Medium Gray	N	25	Y	N	wedge-shaped
CS-04	N 4.5	Medium Dark Gray	N	0	Y	N	wedge-shaped
CS-05	N 4.5	Medium Dark Gray	N	25	Y	Y	irregular
CS-06	N 4.5	Medium Dark Gray	N	50	Y	N	irregular
CS-07	N 3	Dark Gray	N	0	Y	Y	triangular prismatic
CS-08	N 2.5	Grayish Black	N	20	Y	Y	blocky chunk
CS-09	N 4	Medium Dark Gray	N	15	Y	Y	wedge-shaped to trapezoidal
CS-10	N 4	Medium Dark Gray	N	10	Y	Y	triangular blocky slice
CS-11	N 3	Dark Gray	N	0	Y	N	triangular prismatic
CS-12	N 3.5	Dark Gray	Y	15	Y	N	chunky
"	"	"	N	"	"	"	"
CS-13	N 3.5	Dark Gray	N	0	Y	Y	pyramidal chunk
CS-14	N 5	Medium Gray	N	15	Y	N	wedge-shaped
CS-15	N 4	Medium Dark Gray	N	10	Y	N	nearly square blocky slice
CS-16	N 4	Medium Dark Gray	N	25	Y	N	triangular wedge
CS-17	N 5	Medium Gray	N	10	Y	N	thin triangular wedge
CS-18	N 4	Medium Dark Gray	N	25	Y	Y	thick triangular wedge
CS-19	N 4	Medium Dark Gray	N	10	Y	Y	thick wedge
CS-20	N 4	Medium Dark Gray	N	0	Y	N	thin flake
CS-21	N 4	Medium Dark Gray	N	33	Y	Y	triangular chunk
CS-22	N 5	Medium Gray	N	0	Y	Y	triangular chunk
CS-23	N 4	Medium Dark Gray	Y	33	Y	N	triangular prismatic
"	"	"	N	"	"	"	"

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**"Internal" Color Designation** (using GSA Rock Color Chart 1995)	**Color Name ("Internal")** (using GSA Rock Color Chart 1995)	**Presence of Copper Drops**	**Approximate Unworked Surface Area** (%)	**Presence of Microlites** (@ 40x)	**Presence of Banding** (@ 40x)	**Sample Shape**
CS-24	N 4	Medium Dark Gray	N	0	Y	Y	triangular wedge
CS-25	N 4	Medium Dark Gray	N	5	Y	N	triangular slice
CS-26	N 3.5	Dark Gray	Y	15	Y	N	thin triangular wedge
"	"	"	N	"	"	"	"
CS-27	N 3.5	Dark Gray	Y	0	Y	N	rectangular chunk
"	"	"	N	"	"	"	"
CS-28	N 5	Medium Gray	N	0	Y	N	triangular wedge
CS-29	N 4	Medium Dark Gray	N	5	Y	N	thin slice
CS-30	N 4	Medium Dark Gray	N	15	Y	N	moderately thick slice
CS-31	N 4.5	Medium Dark Gray	N	20	Y	N	elongated triangular wedge
CS-32	N 4.5	Medium Dark Gray	N	25	Y	N	elongated triangular wedge
CS-33	N 4.5	Medium Dark Gray	N	5	Y	N	bottom 2/3 of an arrowhead
CS-34	N 2.5	Grayish Black	N	20	Y	N	thin triangular wedge
CS-35	N 2	Grayish Black	N	5	Y	N	thin square wedge
CS-36	N 2.5	Grayish Black	N	5	Y	N	thin squarish wedge
CS-37	N 4	Medium Dark Gray	N	0	Y	N	very thin rhombohedral chip
CS-38	N 3.5	Dark Gray	N	15	Y	N	moderately thick slice
LP-01	N 5	Medium Gray	N	20	Y	N	thin triangular slice
LP-02	N 5	Medium Gray	N	0	Y	Y	triangular prismatic
LP-03	N 3.5	Dark Gray	N	0	Y	N	thin slice
LP-04	N 5	Medium Gray	N	0	Y	N	flat triangular prism
LP-05	N 5	Medium Gray	N	0	Y	N	thin flake
UNI-01	N 4	Medium Dark Gray	N	0	Y	N	triangular prismatic
UNI-02	N 3	Dark Gray	N	15	Y	N	rounded chunk
UNI-03	N 4	Medium Dark Gray	N	5	Y	Y	triangular chip
UNI-04	N 5	Medium Gray	N	0	Y	Y	rectangular thin wedge
UNI-05	n/a	n/a	N	n/a	N	N	triangular chunk
"	"	"	"	"	"	"	"

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	"Internal" Color Designation (using GSA Rock Color Chart 1995)	Color Name ("Internal") (using GSA Rock Color Chart 1995)	Presence of Copper Drops	Approximate Unworked Surface Area (%)	Presence of Microlites (@ 40x)	Presence of Banding (@ 40x)	Sample Shape
UNI-06	n/a	n/a	N	n/a	N	N	triangular elongate wedge
"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"
UNI-07	same	same	N	n/a	N	N	triangular chunk
UNI-08	same	same	N	n/a	N	N	triangular chunk
MO-01	N 4	Medium Dark Gray	N	5	Y	N	pyramidal chunk
MO-02	N 4, N 5	Medium Dark Gray, Medium Gray	N	30	Y	Y	broken chunk
MO-03	N 5	Medium Gray	N	40	Y	N	very large chunk
MO-04	N 5	Medium Gray	N	0	Y	N	thin pyramidal wedge
MO-05	N 5	Medium Gray	N	5	Y	N	thin rectangular chip
VT-01	N 4	Medium Dark Gray	N	20	Y	N	triangular wedge
VT-02	N 4	Medium Dark Gray	N	25	Y	N	elongated triangular wedge
VT-03	N 4	Medium Dark Gray	N	10	Y	Y	triangular wedge
VT-04	N 4	Medium Dark Gray	N	60	Y	N	elongated triangular wedge
VT-05	N 5	Medium Gray	N	15	Y	N	thin triangular wedge
VT-06	N 4	Medium Dark Gray	N	5	Y	N	thick rhombohedral slice
VT-07	N 4.5	Medium Dark Gray	N	10	Y	N	pyramidal chunk
VT-08	N 4.5	Medium Dark Gray	N	5	Y	N	thin triangular wedge
VT-09	N 4.5	Medium Dark Gray	N	5	Y	N	thin elongated triangular chip
VT-10	N 4.5	Medium Dark Gray	N	5	Y	N	elongated pyramidal wedge
VT-11	N 4.5	Medium Dark Gray	N	0	Y	Y	thin elongated triangular chip
VT-12	N 4.5	Medium Dark Gray	N	0	Y	N	thin elongated triangular chip
VT-13	N 4.5	Medium Dark Gray	N	5	Y	N	thin elongated triangular chip
VT-14	N 4.5	Medium Dark Gray	N	0	Y	Y	thin triangular chip
VT-15	N 4	Medium Dark Gray	N	100	Y	Y	irregular chunk

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**"Internal" Color Designation** (using GSA Rock Color Chart 1995)	**Color Name ("Internal")** (using GSA Rock Color Chart 1995)	**Presence of Copper Drops**	**Approximate Unworked Surface Area** (%)	**Presence of Microlites** (@ 40x)	**Presence of Banding** (@ 40x)	**Sample Shape**
VT-16	N 4	Medium Dark Gray	N	50	Y	Y	pyramidal chunk
VT-17	N 4	Medium Dark Gray	N	75	Y	Y	hemi-sphere
VT-18	N 4	Medium Dark Gray	N	30	Y	Y	elongated rectangular chunk
VT-19	N 4.5	Medium Dark Gray	N	5	Y	N	thin rounded chip
VT-20	N 4.5	Medium Dark Gray	N	0	Y	N	thin rhombohedral wedge
VT-21	N 4	Medium Dark Gray	N	5	Y	N	thin wedge
VT-22	N 4	Medium Dark Gray	N	5	Y	N	thin wedge
VT-23	N 4	Medium Dark Gray	N	5	Y	N	thin rectangular chip
VT-24	N 4	Medium Dark Gray	N	5	Y	N	thin rounded chip
VT-25	N 4	Medium Dark Gray	N	0	Y	N	thin rounded wedge
VT-26	N 4	Medium Dark Gray	N	0	Y	N	thin rectangular wedge
VT-27	N 4	Medium Dark Gray	N	5	Y	Y	triangular wedge
VT-28	N 4	Medium Dark Gray	N	25	Y	N	pyramidal chunk
VT-29	N 4	Medium Dark Gray	N	0	Y	N	rhombohedral chunk
VT-30	N 4	Medium Dark Gray	N	5	Y	N	pyramidal chunk
VT-31	N 5	Medium Gray	N	5	Y	Y	thin triangular wedge
VT-32	N 4	Medium Dark Gray	N	5	Y	N	triangular wedge
VT-33	N 4	Medium Dark Gray	N	5	Y	Y	irregular chunk
VT-34	N 4.5	Medium Dark Gray	N	5	Y	N	triangular slice
VT-35	N 4.5	Medium Dark Gray	N	5	Y	N	rhombohedral chip
VT-36	N 4.5	Medium Dark Gray	N	0	Y	N	very thin triangular chip
VT-37	N 4.5	Medium Dark Gray	N	25	Y	Y	thin rectangular wedge
VT-38	N 4.5	Medium Dark Gray	N	0	Y	Y	thin triangular wedge
VT-39	N 3.5	Dark Gray	N	10	Y	N	rhombohedral chunk
VT-40	N 5	Medium Gray	N	10	Y	N	thin rectangular wedge
VT-41	N 4	Medium Dark Gray	N	20	Y	N	rectangular slice
VT-42	N 5	Medium Gray	N	0	Y	N	very thin rectangular wedge
VT-43	N 5	Medium Gray	N	0	Y	N	triangular wedge
VT-44	N 5	Medium Gray	N	0	Y	N	rectangular slice

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Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	Sample Description
CS-01	very abundant microlites (<<0.10mm); banding apparent; microlites are quite irregular in shape and size
"	"
"	"
"	"
"	"
CS-02	abundant microlites of irregular shape (nearly flat, pseudo-hexagonal to prismatic, brown-black to dark brownish-green) & size (~10% >0.10mm<0.33mm, rest <0.10mm); no well-developed banding, but irregular "streaking" caused by the oriented microlites
CS-03	abundant very tiny microlites of irregular shape & size (~5% >0.10mm<0.33mm, rest <<<0.10mm), no apparent orientation; no apparent banding, but some pseudo-bands
CS-04	no apparent banding; very tiny (<<0.10mm) air bubbles, only 1 is ~0.10mm; abundant tiny irregularly shaped microlites w/ larger ones appearing to be aggregates of smaller ones
CS-05	very similar to CS-03, exc. banding more pronounced & much less microxls (only <<1% microxls, >0.10mm); weathered & "leached" surfaces
CS-06	"leached" surface all over; no apparent banding; very tiny microlites (<<0.10mm), often aggregated into "stringers" up to 0.50mm long & very thin; microlites oriented from nearly straight to undulating
CS-07	similar to CS-01, except has some thin bands and 1 microlite ~0.10mm & rest < to <<0.10mm; overall shape suggests possible faceting (smooth faces); has 1 devitrification or crystallization spot on one end (0.50mm in diameter)
CS-08	very tiny microlites of irregular shape and no apparent orientation; similar to CS-05, except banded
CS-09	very similar to CS-08/CS-05
CS-10	very tiny microlites, very similar to CS-09/CS-08/CS-05
CS-11	similar to CS-06, except microlites are smaller (~10% are ~0.10mm) and not aggregated into "stringers"
CS-12	very abundant tiny microlites
"	"
CS-13	very tiny microlites (<0.10mm) which are abundant
CS-14	very similar to CS-03, except no banding; abundant very tiny microlites (<<0.10mm)
CS-15	abundant very tiny microlites (<<0.10mm, w/ ~5% ~0.10mm)
CS-16	abundant very tiny microlites (<<0.10mm)
CS-17	abundant very tiny microlites (<<0.10mm), <1% ~0.10mm psuedo-hexagonal flat
CS-18	abundant very tiny microlites (<<0.10mm); microlites comprise the banding (shadowy banding)
CS-19	abundant very tiny microlites w/ <<1% as ~0.10mm irregular blobs; irregular, non-continuous, shadowy banding
CS-20	very abundant very tiny microlites w/ <<1% aggregated irregular blobs; somewhat "mottled" coloration due to microlites being in close proximity
CS-21	very abundant very tiny microlites; microlites form hazy banding, some bands appear to be pseudo-bands (aggregations of microlites)
CS-22	very abundant very tiny microlites; pseudo-banding (aggregation of microlites)
CS-23	abundant very tiny microlites w/ <<1% as irregular blobs (~0.10mm)
"	"

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	**Sample Description**
CS-24	abundant very tiny microlites; irregular-width pseudo-bands
CS-25	very abundant very, very tiny microlites; microlites loosely associated w/ some pseudo-bands
CS-26 "	very abundant very tiny microlites (<<0.10mm), w/ ~5% ~010mm in size & rounded to irregular in shape; no banding "
CS-27 "	similar to CS-26 "
CS-28	abundant air bubbles (<0.10mm) oriented in 1 direction; few microlites (~0.10mm, w/ 1 being hexagonal & flat, the rest being ellipsoidal to spherical) oriented in same direction as air bubbles
CS-29	very abundant very tiny microlites loosely associated into pseudo-bands
CS-30	similar to CS-26, but w/ thin pseudo-bands
CS-31	very abundant microlites (<<0.10mm); loosely associated into pseudo-bands
CS-32	similar to CS-31
CS-33	similar to CS-31
CS-34	very abundant microlites (<<0.10mm); tightly associated into pseudo-bands in about 1/5 of the piece
CS-35	very abundant microlites (<<0.10mm); associated into tight pseudo-bands
CS-36	very abundant microlites w/ 25% being acicular & remainderer rounded, and ~10% are ~1mm; 1 large tear-shaped air bubble (0.5mm)
CS-37	abundant microlites (~1%, >0.01mm) w/ globular-shaped >> acicular-shaped; pseudo-banding in ~1/12 of piece
CS-38	similar to CS-30
LP-01	similar to CS-29, but no pseudo-banding
LP-02	abundant very tiny microlites loosely associated into bands
LP-03	very few microlites (~10% of these are >0.10mm & irregular-shaped)
LP-04	microlites (>98% were <0.10mm; rest up to 0.20mm & rounded>irregular>pseudo-hex.), w/ very tiny microlites slightly assd into pseudo-bands
LP-05	>98% of the microlites were acicular belonites/trichites, oriented w/ ~50% associated into wispy groups <0.10mm, rest were ~0.15mm globulites or cumulites w/ a few margarites (elongated or bunched up)
UNI-01	abundant microlites (<1% 0.1-0.5mm, globular >>> margarites; rest are <<0.1mm, globular > margarites) are associated into misty bands w/ inter-band areas nearly w/out microlites
UNI-02	abundant microlites (<1% 0.1-0.5mm, rounded to rectangular-globular; rest are <<0.1mm, globular); no pseudo-banding
UNI-03	very similar to UNI-02, except thin, dark, irregular bands composed of tightly spaced very, very tiny microlites
UNI-04	very similar to UNI-03
UNI-05 "	colorless to off-white massive quartz w/ areas of yellow-brown iron-staining & drusy clear quartz & dirt "

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	Sample Description
UNI-06	very fine-grained matrix & lithics; lithics have unclear boundaries (showing partial resorption)
"	"
"	"
"	"
"	"
UNI-07	dark-gray pottery shard w/ design carved into outer (convex) surface; very fine-grained (cannot determine color, size of grains or matrix)
UNI-08	very dark-gray pottery shard w/ design carved into inner (concave) surface; very fine-grained (cannot determine color, size of grains or matrix)
MO-01	very abundant microlites (<10% are 0.1-0.5mm & globular to pseudo-hex.); smaller microlites aggregated into cloudy pseudo-bands
MO-02	hard to see (very thick chunk)--very abundant microlites (<10% are 0.1-0.5mm & globular to pseudo-hexagonal)
MO-03	hard to see (very thick chunk)--very abundant microlites (~10% are 0.1-0.5mm w/ rest <<0.1mm, all globular)
MO-04	very few microlites, few acicular to prismatic microlites (0.5-0.75mm) just under one side of artifact, w/ round air bubbles (<<0.1mm) & pseudo-hexagonal microlites (<<0.1-0.1mm); few spicule-shaped air bubbles (0.1-0.5mm) oriented in 1-direction & associated w/ microlites, 1 large microlite 1.5x1mm w/ some small, rounded air bubbles surrounding it
MO-05	few microlites, <<<0.1mm, w/ <1% up to 0.1mm , all globular
VT-01	very abundant very tiny microlites (~99% <<0.1mm, globular, w/ <1% up to 0.1mm, globular to flatish pseudo-hexagonal
VT-02	very abundant tiny microlites
VT-03	very abundant tiny microlites (~98% <<0.1mm globular > margarites > acicular, w/ ~2% up to 0.2mm, globular, flatish pseudo-hexagonal & irregular); banding consists of extremely tiny dark microlites
VT-04	similar to VT-01
VT-05	very similar to VT-03, but banding irregular & "wispy"
VT-06	very abundant microlites (~99% <<0.1mm globular, rest up to 0.1mm globular & flat pseudo-hex.); pseudo-banding irreg., pervasive & "wispy"
VT-07	similar to VT-01
VT-08	similar to VT-07; no pseudo-banding
VT-09	similar to VT-08
VT-10	similar to VT-08
VT-11	similar to VT-05
VT-12	similar to VT-11, but tiny microlites globular, while larger ones acicular (up to 0.5mm) & oriented w/ the pseudo-banding, some larger microlites look brownish in color
VT-13	abundant microlites (~90%<<0.1mm & globular, rest are 0.25-0.1mm acicular > ~0.1mm & irregular & pseudo-hexagonal); elongated air bubbles (0.1-0.5mm) oriented w/ the acicular microlites
VT-14	1/2 of artifact has abundant microlites (~90% <<0.1mm globular & acicular, rest are irregular/globular/pseudo-hexagonal & oriented in 1-direction); other 1/2 of artifact is cloudy-looking, and has very abundant microlites (up to 0.2mm globular > acicular) w/ elongated air bubbles (up to 0.2mm) oriented w/ them; the halves are separated by a cloudy band of very, very tiny black globular microlites
VT-15	very similar to VT-14, but no air bubbles

Table C-2, continued. Artifact Descriptions.

Sample # (this Author's label)	Sample Description
VT-16	very similar to VT-14, but no air bubbles
VT-17	very similar to VT-14, but no air bubbles
VT-18	very similar to VT-14, but no air bubbles
VT-19	cloudy w/ abundant microlites (~99% <<0.1mm & globular, rest up to 0.1mm & globular/flat hexagonal)
VT-20	very abundant microlites (~99% <<0.1mm globular > acicular, rest up to 0.1mm & globular/flat hexagonal) oriented in 1-direction
VT-21	very similar to VT-20, but no acicular microlites
VT-22	abundant microlites (>99% <<0.1mm, rest up to 0.1mm & globular)
VT-23	very abundant microlites (~100% <<0.1mm & globular, rest up to 0.2mm & globular/irregular); elongated to tear-shaped air bubbles (up to 0.2mm) & oriented in 1-direction
VT-24	very similar to VT-21
VT-25	very similar to VT-21
VT-26	microlites (~90% <0.1mm & glob., rest up to 0.2mm & glob./hex) not oriented, w/ few wispy agglomerations of v. tiny microxls
VT-27	very similar to VT-26
VT-28	microlites (~90% <0.1mm & globular, rest up to 0.2mm & globular/hexagonal) were oriented in 1-direction, w/ a few wispy agglomerations of very tiny microlites into irregular dark bands
VT-29	microlites (~100% <0.1mm & globular, rest up to 0.2mm & globular/hexagonal) were not oriented, w/ a few wispy agglomerations of very tiny microlites into wispy irregular dark bands
VT-30	similar to VT-29, but microlites not oriented, and no pseudo-banding
VT-31	very similar to VT-20, but w/ cloudy thin bands
VT-32	very similar to VT-30
VT-33	very abundant microlites (~99% <<0.1mm & globular, aggregated into dark bands, oriented in 1-direction; rest are up to 0.1mm & globular)
VT-34	very abundant microlites (~99% <<0.1mm & globular in a cloudy matrix; rest are up to 0.1mm & globular & oriented in 1-direction)
VT-35	very abundant microlites (~99% <<0.1mm & globular; <1% up to 0.2mm & globular > margarites) w/ some wispy, irregular pseudo-banding
VT-36	very similar to VT-35
VT-37	very similar to VT-14
VT-38	abundant microlites (100% <<0.1mm globular), w/ ~1/2 aggregated into dark, cloudy gray irregular bands
VT-39	very abundant microlites (~99% <<0.1mm globular, rest up to 0.1mm globular & flat pseudo-hexagonal), cloudy matrix
VT-40	very abundant microlites (100% <0.1mm globular), w/ some aggregated into irregular wavy "bands"
VT-41	very similar to VT-34, but w/ 1 large microlite (0.5mm, flat pseudo-hexagonal)
VT-42	abundant microlites (~99% <<0.1mm globular, rest up to 0.2mm flat pseudo-hexagonal > globular > irregular), oriented in 1-direction
VT-43	very similar to VT-39
VT-44	very similar to VT-39

Geological Society of America. 1995. *GSA Rock Color Chart, with Genuine Munsell Color Chips*, 8th ed. 14 pages, inc.6 plates of color chips.

APPENDIX D
OBSIDIAN SOURCE DATA

This Appendix discusses the chemical data utilized here for the obsidian sources involved in this study, why this data was chosen, and how the source data was utilized in comparison against the obsidian debitage chemical data. Also discussed is the process by which obsidian sources were eliminated from consideration as potential source materials for the 96 debitage pieces, and how the final provenance determinations were made.

Obsidian Sources Included in This Study

As detailed in Chapter 3, numerous sources of obsidian have been identified in Central America, Mexico, South America, and North America. Theoretically, any of these sources may have been the source material from which any of the 96 obsidian debitage pieces studied here had been formed. However, as it is more likely that those obsidian sources located closest to the archaeological sites involved in this study would be represented in this set of 96 obsidian debitage pieces, the sources located in Central America were of prime importance. After conducting the comparisons of elemental compositions of the 96 debitage pieces against that of the 20 known (and analyzed) Central American sources, 1 debitage piece remained without provenance, thus a select number (11 out of the 66 known) of Mexican sources were also compared (see Chapter 5, and below). No other sources were compared after this, as the pieces are believed to be as fully provenanced as possible (see Chapter 5, and below).

Central American Obsidian Sources

There are 21 obsidian sources in Central America (listed by country, from closest to the archaeological sites studied here to farthest from them): 3 in Nicaragua (2 are "known," with samples collected and analyzed, and 1 "prospective," with no known samples or chemical analyses), 6 in Honduras, 1 in El Salvador, and 11 in Guatemala (Aoyama et al. 1999; IAOS 2007; Nelson et al. 1983; Sheets et al. 1990; Stross et al. 1976; Stross et al. 1992). See Chapter 3 for more details and a map of locations (Figure 4), and Table D-1 for a summary of the chemical data utilized here (20 of the 21 sources had chemical data). These sources range in distance to the archaeological sites from the closest at ~60 km (~40 miles), the Luisitio, Nicaragua, source, to the farthest at ~690 km (~430 miles), the Palo Gordo, Guatemala, source (Aoyama et al. 1999; IAOS 2007; Nelson et al. 1983; Sheets et al. 1990; Stross et al. 1976; Stross et al. 1992).

Mexican Obsidian Sources

Also described more fully in Chapter 3, there are at least 66 known obsidian sources in Mexico, ranging from as close to the archaeological sites as the State of Veracruz (~1600 km, or ~1000 miles, the Pico de Orizaba source), to as far from them as the State of Sonora (~3600 km, or ~2250 miles, the Los Vidrios source) (Cobean et al. 1971; Ericson and Kimberlin 1977; Glascock et al. 1988; Harris 1986; IAOS 2007; Stross et al. 1976; Zeitlin and Heimbuch 1978). However, only 11 have been determined to be source materials for Central American artifacts (see for example: Moholy-Nagy 2003), and thus only these were included here (see Table D-1); locations not shown.

South and North American Obsidian Sources

Numerous other sources of obsidian have been identified throughout both South America (at least 41 sources: Barnes et al. 1970; IAOS 2007) and North America (at least 379 sources: IAOS 2007) (see Chapter 3 for more details). However, none of these sources are included in this study, as their distances to the archaeological sites are even greater than that for the Mexican sources: South American sources ranged from ~1700 km, or ~1060 miles (the Rio Hondo source, Colombia), to ~7700 km, or ~4800 miles (the Seno Otway source, Chile) (Barnes et al. 1970; IAOS 2007), and North American sources ranged from ~3150 km, or ~1960 miles (the Rio Grande Gravels source, Texas), to ~8250 km, or ~5150 miles (the Batza Tena source, Alaska) (IAOS 2007). Thus it is extremely unlikely that any of these obsidian sources served as source materials for the debitage pieces studied here; locations not shown.

Factors for Choosing the Obsidian Source Chemical Data

The chemical data for the obsidian sources studied here were selected for inclusion in this study based on 3 main factors, with the first 2 being of the greatest importance, and the 3rd of only somewhat lesser importance: 1) the laboratory (thus analytical method used for) performing the chemical analyses; 2) how the analytical data was presented; and, 3) how long ago the analyses were performed. This last factor is essentially that of time and technology; instrumental detection limits, and indeed, instrumental methods, have changed greatly over time. Detection limits not possible just 20-25 years ago (parts per million (ppm) for many elements, and for some elements parts per billion (ppb)) are now quite routine, and expected to be attained routinely. Thus, chemical data ~20 years old and older were avoided, if at all possible. However, in a minimal number of cases, some chemical data was included that might be considered somewhat dated (Glascock et al. 1988; Vogt et al. 1982), but was utilized here as the analyses were obtained via NAA under supervision of Dr. Glascock. Additionally, the only chemical data that could be found for 2 obsidian sources was up to 31 years old (Nelson et al. 1983, for Cruz de Apan, Guatemala; Stross et al. 1976, for Santa Ana Volcano, El Salvador), and thus were used for lack of obtaining more up-to-date data.

Analyses performed via Neutron Activation Analysis (NAA), and especially those at the Missouri University Research Reactor (MURR) laboratory under supervision of Dr. Michael Glascock, Senior Scientist and Group Leader, Archaeometry Laboratory, University of Missouri, Columbia, Missouri., were of prime importance in this study, thus much preferred over analyses performed via other analytical techniques, for a number of reasons. MURR NAA, under Dr. Glascock's guidance, has not only become an increasingly important analytical and research resource for obsidian (and other) provenance studies since 1979 (University of Missouri-Columbia 2007; see also for example: Craig et al. 2007; Glascock et al. 1988; Glascock 1999; Jennings and Glascock 2002; Vogt et al. 1982), but Dr. Glascock has also graciously collaborated in this current study by providing some chemical data (generated via NAA at MURR) for use here (Michael Glascock, written communication 4/22/0997). In addition, NAA is one of the most sensitive techniques capable of qualitative and quantitative elemental analysis for numerous elements (many being trace elements) simultaneously, with sensitivities for many elements superior than that obtained by any other technique, and is still one of the primary analytical methods used by the National Institute of Standards and Technology for certifying the concentration of elements in Standard Reference Materials (University of Missouri-Columbia 2007). However, in a minimal number of cases, chemical data had either not been obtained via NAA (either at MURR or another laboratory), or such data could not be obtained by this researcher, and is discussed.

Chemical data presented in the form of single sample analyses were much preferred over that presented as averages (means) or ranges. This was especially important for the Central American obsidian sources, as these were of prime interest in this study, being located closest to the archaeological sites and thus most likely as source materials for the debitage pieces. "Grouped" data (data presented as a range of values) for the Mexican sources was utilized at first, as these sources were of lesser importance. Also, if any were found to be close in composition to that of any of the debitage pieces, individual data would be sought, although this was found not to be necessary. Analyses of single samples could be more easily plotted on element versus element plots than data presented in the form of averages or means (+/- some amount of deviation) for some number of samples, or ranges (minimums and maximums) for some number of samples. In order to plot "averaged" data, it was necessary to calculate the "possible minimum" and "possible maximum" for each element reported in such a manner. This was done by using the given average (or mean) for each element as the mean, subtracting the given deviation for each element from such mean to yield the "possible minimum" for each element, and then likewise adding the deviation to the mean to yield the "possible maximum" for each element. In order to plot "ranged" data, the given minimums and maximums for each element reported in this manner were used to calculate their means. More important than easier plotting, data presented in the form of averages (means) or ranges may not give a true sense for how much each sample's analytically-measured value varies from each other in that data set, or from all other samples for that obsidian source. Having each individual obsidian source sample's chemical analysis to compare to all others for that obsidian source allows researchers to gain a better understanding of the extent of variation for that obsidian source, and is of high importance. Having such individual data is essential for accurate mathematical manipulation of data, such as calculating elemental ratios, as well. However, in a minimal number of cases (discussed below), individual sample data was either not available, or not obtainable, and the calculations mentioned above were employed. When the analytical data for the 96 obsidian debitage pieces were added to each element versus element plot already containing the obsidian source sample data points (especially those representing single samples), the "true" relationships of debitage pieces to source samples were more realistically depicted.

Chemical Data for the Obsidian Sources Utilized in This Study

The compositional data for the 96 obsidian debitage pieces were obtained as part of this study, as discussed in Appendices A and C, and is given in Table C-1 (Appendix C). As discussed in Appendix B, Analytical Data and Tables section, the debitage pieces had been analyzed for a total of 42 elements. However, the chemical analyses for 14 of these elements were unusable (at or below detection limits), leaving a data set for 28 elements (Al, Ba, Ca, Ce, Cr, Cs, Cu, Fe, K, Ga, La, Li, Mg, Mn, Na, Nb, Ni, Pb, Rb, Sr, Ta, Th, Tl, U, V, W, Y, and Zn). Although trace elements were intended to be of prime interest here, potentially all 28 of these elements may be scrutinized during the course of this study. Therefore, the compositional information gathered for the potential obsidian sources would ideally also have data for these same 28 elements to allow for comparison, if needed. However, the compositional data gathered for the sources did not include quite as many of these same 28 elements as hoped (NAA at MURR typically measures for 27 elements in geological materials: Ba, Ce, Cl, Co, Cs, Dy, Eu, Fe, Hf, K, La, Lu, Mn, Na, Nd, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, U, Yb, Zn, and Zr; Braswell 1996:127-128), with 16 in all (Al, Ba, Ca, Ce, Cs, Fe, K, La, Mn, Na, Rb, Sr, Ta, Th, U, and Zn); see Table D-1. These 16 elements were sufficient for determining some important information in this study, such as definitive provenance for 5 of the 96 obsidian debitage pieces (see Chapter 5), though perhaps not enough to have fully determined all possible information, as 91 of the 96 pieces remain without definitive provenance (although they have been as fully provenanced here as possible, given these elements; see Chapter 5).

Sources, and Some Limitations, of the Obsidian Source Chemical Data

The compositional data utilized for the obsidian sources included in this study were gleaned from a number of sources, as discussed below, with these data summarized and presented as ranges of composition by source in Table D-1. In a number of cases, the amount of data available for a particular obsidian source was limited, some extremely so. Such limited data puts many limitations on the statistical analysis, and interpretation, of such data (see for example discussions: Glascock 1994; Glascock et al. 1998; Shackley 2005). However, these limited data were to be used here in a more statistically-simple manner, that of comparing compositions of individual samples to one another in element versus element plots to visually assess how the debitage data falls in relation to that of the data for the sources. Interestingly, even the limited amount of data available for some of these sources was sufficient to make decisions with regard to elimination, and likely the same decisions would result if a greater quantity of data would be available to scrutinize.

Following are listed those Central American obsidian sources for which there was very to extremely limited compositional data available, but with individual analyses given. The 2 known Nicaraguan obsidian sources, "Luisitio" and "Lake Nicaragua" (abbreviated LU and LN here), with just 3 analyses for LU (via XRF) and 4 for LN (2 via NAA, 2 via XRF), as found in Sheets et al. (1990), with the same data also presented in Stross et al. (1992). The single El Salvadoran source, Santa Ana Volcano (SAV), with just 1 analysis (via XRF) found in Stross et al. (1976). The Honduran source, El Paraiso (EP), with just 1 analysis (via NAA) found in Aoyama et al. (1999). The Guatemalan source, Cruz de Apan (CDA), with just 2 analyses (via XRF) found in Nelson et al. (1983). The Guatemalan source, San Lorenzo (SL), with just 2 analyses (via NAA), one found in Vogt et al. (1982), the other in Cobean et al. (1991).

Following are listed those Central American obsidian sources for which there was limited compositional data available, but with "grouped" analytical results given (means for a various number of analyses, +/- some deviation from those means). The Honduran sources, Agua Helada (AH), Agua Sucia (AS), and San Luis (SLU), with means for 5, 5, and 9 analyses (via NAA), respectively, found in Aoyama et al. (1999). Both individual data (2 NAA analyses in Vogt et al. 1982), and grouped data (the mean of 2 NAA analyses in Cobean et al. 1991) were found for the Guatemalan source, Palo Gordo (PG).

The compositional data for the remaining Central American obsidian sources are all comprised of individual analyses, and listed below by country and obsidian source. The Honduran sources: Güinope (GUIN), with 4 analyses (via NAA) provided by Dr. Michael Glascock, Senior Scientist and Group Leader, Archaeometry Laboratory, MURR

(Michael Glascock, written communication 4/22/1997), and 2 more analyses (1 via NAA, 1 via XRF) found in Sheets et al. (1990), with these same 2 analyses also presented in Stross et al. (1992); and, La Esperanza (ESP), with 11 analyses (via NAA) provided by Dr. Michael Glascock, MURR (Michael Glascock, written communication 4/22/1997). The Guatemalan sources: El Chayal (EC), with 14 analyses (via NAA) provided by Dr. Michael Glascock, MURR (Michael Glascock, written communication 4/22/1997); Ixtepeque (IXT), with 4 analyses (via NAA) provided by Dr. Michael Glascock, MURR (Michael Glascock, written communication 4/22/1997); Jalapa (JAL), with 1 analysis (via NAA) found in Cobean et al. (1991), and 5 analyses (via NAA) in Braswell (1996); Laguna de Ayarza (LDA)/Media Cuesta (MC), already pre-grouped together as "one geochemical source," with 25 analyses (via NAA) found in Braswell (1996); San Bartolomé Milpas Atlas (SBMA), with 10 analyses (via NAA) found in Braswell (1996); San Martín Jilotepeque (SMJ), with 32 analyses (via NAA) provided by Dr. Michael Glascock, MURR (Michael Glascock, written communication 4/22/1997); and, Sansare (SNS), with 10 analyses (via NAA) found in Braswell (1996).

Although the Mexican sources were of lesser concern here, NAA data was emphasized. And though no great effort was expended in seeking individual analyses, some are included. The data is listed here by source (with analytical method): Altotonga (NAA: Cobean et al. 1991); Guadalupe Victoria (NAA and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS): Carballo et al. 2007; NAA: Cobean et al. 1991, and Vogt et al. 1982); Otumba (NAA and LA-ICP-MS: Carballo et al. 2007; NAA: Cobean et al. 1991); Pachuca (NAA and LA-ICP-MS: Carballo et al. 2007; NAA: Cobean et al. 1991, and Glascock et al. 1988); Paredón (NAA and LA-ICP-MS: Carballo et al. 2007; NAA: Cobean et al. 1991); Pico de Orizaba (NAA: Cobean et al. 1991, and Vogt et al. 1982); Tulancingo (NAA and LA-ICP-MS: Carballo et al. 2007; NAA: Cobean et al. 1991, and Glascock et al. 1988); Ucareo (NAA and LA-ICP-MS: Carballo et al. 2007); Zacuáltipan (NAA and LA-ICP-MS: Carballo et al. 2007; NAA: Glascock et al. 1988); Zaragoza (NAA and LA-ICP-MS: Carballo et al. 2007; NAA: Cobean et al. 1991); and, Zinapécuaro (NAA: Cobean et al. 1991, and Vogt et al. 1982). Note that, although LA-ICP-MS data was included in this set, these analyses were not emphasized.

Methodology for Eliminating Obsidian Sources as Potential Source Materials for the Obsidian Artifacts Studied Here

The methodology followed in this study for determining the provenance of the 96 obsidian debitage pieces involved in a number of steps, mainly regarding evaluating trends seen the data (debitage pieces and potential sources). One of the most important issues involved the exact criteria by which an obsidian source was eliminated as a potential source material. Therefore, the chemical data (and element versus elements plots) were scrutinized carefully, using numerous elements, before final decisions regarding elimination of sources as potential source materials were made.

Method for Evaluating Data Trends

The first step involved getting an initial look at how the obsidian debitage pieces plotted in relation to 5 important Central American obsidian sources (El Chayal (EC), Ixtepeque (IXT), and San Martín Jilotepeque (SMJ), Guatemala, and Güinope (GUIN), and La Esperanza (ESP), Honduras), which have often been determined to be the source materials for Central American artifacts (see Chapter 3). For this, a number of element versus element plots (especially using trace elements) were prepared by plotting the chemical data for all individual samples used for these 5 sources, then adding the chemical data for the 96 individual debitage pieces to these plots. With these initial elemental plots, it could be seen that a number of debitage pieces repeatedly associated (for a number of elements, especially trace elements) with the same Central American sources (1 piece with ESP, and 4 pieces with IXT), or the same grouping of sources of similar chemistry (90 pieces with EC plus GUIN), and 1 piece with none at all (piece CS-37); no pieces tended to repeatedly associate with SMJ. Further, nearly all plots involving at least 1 trace element revealed separations, or gaps, between these debitage piece "groupings," or associations, such that there were compositional gaps between them (see Figures 5 and 6, Chapter 3, as examples). Another way to look at this might be that there are compositional gaps between the source "envelopes" (as delineated by the source sample populations) for these 4 sources with which debitage pieces were associating (ESP, IXT, and the grouping of EC/GUIN).

The second step involved adding all remaining Central American sources to these elemental plots to determine how the debitage pieces fell in relation to all these potential source materials. The picture grew a bit more complicated, although the same basic associations seen in the initial plots held: the same single piece with ESP, the same 4 pieces with IXT, the same single piece unassociated, and the same 90 pieces associated with a grouping of EC and GUIN, although this grouping now included the Jalapa, Guatemala (JAL), source. However, not only did quite a few of these newly-added sources have elemental compositions that were higher or lower (some significantly) than that of the debitage pieces, but a number of these sources repeatedly plotted in the "compositional gaps" between the debitage pieces or groupings of pieces with sources.

The third step involved adding a select number of Mexican sources (11 out of the 66 known Mexican obsidian sources; see Chapter 3) to these elemental plots to see if the single unassociated piece (CS-37) would associate with any of these. Most of these obsidians had compositions far too different from any of the debitage pieces studied here, even that of CS-37, and were eliminated as possible source materials right away, as discussed below. Just 2 of these sources had compositions somewhat similar to CS-37: Guadalupe Victoria, State of Puebla, and Pico de Orizaba, State of Veracruz. Guadalupe Victoria appeared to be slightly more similar to CS-37 in composition, although still not a particularly close match, and this association was thus deemed "tentative." In addition, there is reason to believe that CS-37 likely may have been derived from an as-yet unidentified Central American obsidian source (see Chapter 3).

The fourth, and final, step performed here in determining the provenance of the obsidian debitage pieces was that of double-checking the apparent associations found via element versus element plots, using the elemental data. This was performed to ensure that the associations of certain pieces of debitage with certain sources, and other trends "seen" in the plots were indeed valid.

Usefulness of Elemental Data

The elements deemed of greatest importance regarding elimination of possible obsidian sources at the outset were the trace elements, although nearly all other elements for which there was data were also utilized, as a number of sources had limited chemical data and 3 sources (EC, GUIN, and JAL) had very similar chemistry. As mentioned earlier in this Appendix, chemical data for 28 elements (Al, Ba, Ca, Ce, Cr, Cs, Cu, Fe, K, Ga, La, Li, Mg, Mn, Na, Nb, Ni, Pb, Rb, Sr, Ta, Th, Tl, U, V, W, Y, and Zn) was obtained here for the 100 artifacts, and chemical data for 16 elements (Al, Ba, Ca, Ce, Cs, Fe, K, La, Mn, Na, Rb, Sr, Ta, Th, U, and Zn; see Table D-1) was gathered and utilized here for the obsidian sources. The 16 elements, and how each compared with the obsidian debitage data, are summarized below.

Aluminum (Al) was not important in this study: The lowest obsidian debitage value (excepting piece CS-37) was 55800 ppm, the highest 92300 ppm; Only 2 Central American sources had data for Al, and both were entirely within the range of the debitage data; There were no Al data for any of the 11 Mexican sources.

Barium (Ba) was an important element in this study: The lowest debitage value (less piece CS-37) was 819 ppm, and the highest 1210 ppm; Of the 19 Central American sources, 6 had Ba values lower to much lower than this range, 3 had values starting somewhere within this range and ranging into either lower (1) or higher (2) values, and 10 were entirely within the range of debitage data; Of the 11 Mexican sources, 8 had Ba values lower to much lower, 2 had values starting within the debitage data range and ranged into lower values, and 1 was entirely within the debitage data range.

Calcium (Ca) was important in this study regarding only 1 source: Luisitio, Nicaragua, for which only an extremely limited amount of chemical data was available;. The lowest debitage value for Ca (less piece CS-37) was 5530 ppm, and the highest 10000 ppm; Luisitio was extremely high, at ~50000-70000 ppm; Only 1 other source studied here with Ca data was Santa Ana Volcano, El Salvador, which was entirely within the debitage data range; None of the 11 Mexican sources had Ca data.

Cerium (Ce) was of limited importance here: The lowest debitage value (less piece CS-37) was 39.0 ppm, the highest 59.1 ppm; Of the 19 Central American sources, 2 had no Ce data, 2 had lower Ce values, 1 had a higher Ce value, 3 started within the debitage data range and ranged into either lower (1) or higher (2) values, and 11 were entirely within the debitage data range; Of the 11 Mexican sources, 2 had lower to much lower Ce values, 7 had higher to much higher Ce values, 1 started within the debitage data range and went lower, and 1 was entirely within the debitage data range.

Cesium (Cs) was of great importance in this study: The lowest debitage value (less CS-37) was 2.42 ppm, the highest 8.89 ppm; Of the 19 Central American sources, 3 had no Cs data, just 1 started within the debitage data range and went lower, and 15 appeared to be entirely within the debitage data range; Further scrutiny of the data and elemental plots revealed that 7 of these fell into the compositional gaps between debitage piece groupings; Of the 11 Mexican sources, 1 had a higher Cs value, 2 started within the debitage data range (1 went lower, 1 higher), and 8 appeared to be entirely within the debitage data range, although 6 of these were revealed to also fall into the compositional gaps between debitage piece groupings.

Iron (Fe) was important in this study: The lowest debitage value (less CS-37) was 7170 ppm, the highest 15300 ppm; Of the 19 Central American sources, 4 had lower Fe values, 1 had a much higher Fe value, 1 started within the debitage data range and went lower, and 13 were entirely within the debitage data range; Of the 11 Mexican sources, 2 had lower Fe values, 1 had a higher Fe value, 3 started within the debitage data range (2 went lower, 1 higher), and 5 were entirely within the debitage data range.

Potassium (K) was of limited importance here: The lowest debitage value (less CS-37) was 28100 ppm, the highest 43200 ppm; Of the 19 Central American sources, 2 had no K data, 1 had a lower K value, 1 had a higher K value, 3 started within the debitage data range (1 went lower, 2 higher), and 12 were entirely within the debitage data range; Of the 11 Mexican sources, 3 started within the debitage data range and went higher, and 8 were entirely within the debitage data range.

Lanthanum (La) was important in this study: The lowest debitage value (less CS-37) was 22.1 ppm, the highest 34.2 ppm; Of the 19 Central American sources, 3 had no La data, 1 had a lower La value, 1 had a much higher La value, 1 started within the debitage data range and went lower, and 13 were entirely within the debitage data range; Of the 11 Mexican sources, 3 had lower La values, 6 had higher, 1 started within the debitage data range and went higher, and 1 was entirely within the debitage data range.

Manganese (Mn) was important in this study: The lowest debitage value (less CS-37) was 387 ppm, the highest 597 ppm; Of the 19 Central American sources, 1 had no Mn data, 3 had lower Mn values, 6 had higher, 1 started within the debitage data range and went higher, and 8 were entirely within the debitage data range; Of the 11 Mexican sources, 6 had lower to much lower Mn values, 1 had a much higher Mn value, 2 started within the debitage range and went lower, and 2 were entirely within the debitage range.

Sodium (Na) was of limited importance here: The lowest debitage value (less CS-37) was 20300 ppm, the highest 33800 ppm; Of the 19 Central American sources, 2 had no Na data, 2 had lower Na values, 2 started within the debitage data range and went higher, and 13 were entirely within the debitage data range; Of the 11 Mexican sources, 1 had a higher Na value, 1 was within the debitage data range and went higher, and 9 were entirely within the debitage data range.

Rubidium (Rb) was important here: The lowest debitage value (less CS-37) was 88.5 ppm, the lowest 182 ppm; Of the 19 Central American sources, 1 had no Rb data, 2 had lower Rb values, and 16 appeared to be entirely within the debitage data range, with further scrutiny revealing that 5 of these fell into the compositional gaps between debitage piece groupings; Of the 11 Mexican sources, 4 started within the debitage data range (1 went lower, 3 higher), and 7 appeared to be entirely within the debitage data range, although 2 of these also fell into the compositional gaps.

Strontium (Sr) was important here: The lowest debitage value (less CS-37) was 140 ppm, the highest 216 ppm; Of the 19 Central American sources, 4 had no Sr data, 4 had lower to much lower Sr values, 2 had higher, 4 started within the debitage data range (3 went lower, 1 higher), 1 showed an extreme range from lower than the lowest debitage data value (less CS-37) to higher than the highest debitage data value, and 4 were entirely within the debitage data range; None of the 11 Mexican sources had Sr data.

Tantalum (Ta) was of limited importance here: The lowest debitage value (less CS-37) 0.756 ppm, highest 1.36 ppm; Of the 19 Central American sources, 3 had no Ta data, 2 had lower Ta values, 3 had higher, 2 started within the debitage data range and went lower, and 9 were entirely within the debitage data range; Of the 11 Mexican sources, 5 had higher to much higher Ta values, 4 started within the debitage data range (1 went lower, 3 higher to much higher), and 2 were entirely within the debitage range.

Thorium (Th) was important in this study: The lowest debitage value (less CS-37) was 6.80 ppm, highest 14.6 ppm; Of the 19 Central American sources, 3 had no Th data, 2 had lower Th values, and 14 appeared to be entirely within the debitage data range, although further scrutiny revealed 7 of these to fall into the compositional gaps between debitage piece groupings; Of the 11 Mexican sources, 5 had higher Th values, 2 started within the debitage data range (1 went lower, 1 higher), and 4 appeared to be entirely within the debitage data range, though 1 of these fell into a compositional gap.

Uranium (U) was important in this study: The lowest debitage value (less CS-37) was 2.23 ppm, highest 5.50 ppm; Of the 19 Central American sources, 3 had no U data, 1 had a lower U value, and 15 were entirely within the debitage data range; Of the 11 Mexican sources, 1 had a higher U value, 6 started within the debitage data range (1 went lower, 5 higher), and 4 were entirely within the debitage data range.

Zinc (Zn) was of lesser importance here: The lowest debitage value (less CS-37) was 31.2 ppm, highest 72.0 ppm; Of the 19 Central American sources, 4 had no Zn data, 2 had lower Zn values, 3 started within the debitage data range and went lower, and 10 were entirely within the debitage data range; Of the 11 Mexican sources, 1 had a lower Zn value, 2 had higher, 1 started within the debitage data range and went lower, and 7 were entirely within the debitage data range.

Evaluation of Source Data Trends and Elimination of Obsidian Sources

As just discussed, some of the 16 elements were more useful or important than others regarding evaluation of the 19 Central American and 11 Mexican obsidian sources as potential source materials for the 96 obsidian debitage pieces. This usefulness translates into how effective a given element is in: 1) delineating between obsidian sources; and, 2) revealing associations between obsidian artifacts and obsidian sources. In a given data set, it is hoped that at least enough elements will have been analyzed such that both pieces of information (delineation between sources, and definitive associations of artifacts with sources) will be obtained. However, the needed information may not always be obtained, for a number of reasons, such as perhaps not enough elements (or not the "right" elements) were analyzed for the artifact(s), or not enough chemical data exists for the source to allow for a proper comparison against it, or the source(s) of the artifacts may yet be unidentified, or the range of composition for a source is larger than has been previously analyzed. The first, third, and fourth situations may be likely reasons for a number of obsidian debitage pieces remaining without definitive provenance in this current study (see Chapter 5).

Below are summarized some important trends regarding the chemical information gathered for the obsidian sources studied here (see Table D-1 for this chemical data). These trends are listed by country and obsidian source. The most important trends, those that led to decisions regarding elimination of obsidian sources as potential source materials for the 96 obsidian debitage pieces studied here are italicized to stand out. Although nearly every element (except Al, and Na for most cases) was ultimately utilized in these eliminations, the most important elements were the trace elements (Ba, Ce, Cs, La, Rb, Sr, Th, and U, and even Ta and Zn), with several other elements (Ca, Fe, K, and Mn) playing important roles in certain cases. With this data set of 16 elements, all but 5 of the 19 known Central American obsidian sources are eliminated as possible source materials for the obsidian debitage pieces studied here, plus 10 of the 11 Mexican obsidian sources also compared.

Nicaragua: Luisitio (LU): extremely limited data set (just 4 elements studied here); *low Ce*; *extremely high Ca and Fe*; no data for Al, Cs, K, La, Mn, Na, Rb, Sr, Ta, Th, U, or Zn; Lake Nicaragua (LN): *low La, Rb, Ta, Th, and U*; *high Ba and Mn*; ranging to low values for Ce, Cs, and K; no data for Ca, Sr, or Zn.

Honduras: Güinope (GUIN): ranging to high values for K; no data for Al or Ca; La Esperanza (ESP): ranging to low values for Ba and Sr; no data for Al or Ca; Agua Helada (AH): *low Ba, Fe, Mn, Sr, and Zn*; *high Ta*; ranging to high values for Ce and K; *Cs values between debitage groupings*; no data for Al or Ca; Agua Sucia (AS): *low Ba and Sr*; *high Mn and Ta*; ranging to high Ce; *Rb and Th values between debitage groupings*; no data for Al or Ca; El Paraiso (EP): *low Ba, Mn, and Na*; *high Ce, K, La, and Ta*; *Rb and Th values between debitage groupings*; no data for Al or Ca; San Luis (SLU): *low Ba, Mn, and Sr*; ranging to low Fe; *Cs values between debitage groupings*; no data for Al or Ca.

El Salvador: Santa Ana Volcano (SAV): very limited data set (just 7 elements studied here); *low Ba, K, and Sr*; no data for Al, Ce, Cs, La, Na, Ta, Th, U, or Zn.

Guatemala: Cruz de Apan (CDA): very limited data set (just 6 elements studied here); *low Na and Rb*; *high Mn and Sr*; no data for Al, Ca, Ce, Cs, K, La, Ta, Th, U, or Zn; El Chayal (EC): *low Fe*; *high Mn*; ranging to low Sr and Zn; *Th values between debitage groupings*; no data for Al or Ca; Ixtepeque (IXT): low Zn; no data for Al and

Ca; Jalapa (JAL): no data for Al or Ca; Laguna de Ayarza/Media Cuesta (LDA/MC): *high Mn*; *Sr both lower and higher than debitage range*; ranging to high Na; *Cs and Rb values between debitage groupings*; no data for Al or Ca; Palo Gordo (PG): *high Mn*; ranging to low Ta; ranging to high Ba and Na; *Cs and Th values between debitage groupings*; no data for Al, Ca, or Sr; San Bartolomé Milpas Atlas (SBMA): *low Ta*; ranging to low Sr; *Cs, Rb, and Th values between debitage groupings*; no data for Al or Ca; San Lorenzo (SL): *low Ce and Fe*; ranging to low La, Ta, and Zn; *Cs and Th values between debitage groupings*; no data for Al or Ca; San Martín Jilotepeque (SMJ): *low Fe*; ranging to low Zn; ranging to high Sr; *Cs and Rb values between debitage groupings*; no data for Al or Ca; Sansare (SNS): *low Ba*; *high Sr*; ranging to high Mn; *Th values between debitage groupings*; no data for Al or Ca.

Mexico (note that there was no data for any of the 11 Mexican sources for Al, Ca, or Sr): Altotonga: *low Ba and Mn*; *high Ce, La, Ta, and Th*; ranging to high U; Guadalupe Victoria: *low Fe and La*; *high Ce*; ranging to low Rb, Ta, and Zn; *Cs values between debitage groupings*; Otumba: *low Ba*; ranging to low Mn; *Cs, Rb, and Th values between debitage groupings*; Pachuca: *low Ba*; *high Ce, La, Mn , Na, Ta, and Zn*; ranging to low Cs; ranging to high Fe, K, Rb, Th, and U; Paredón: *low Ba and Mn*; *high Ce, La, Ta, and Th*; ranging to high U; *Cs values between debitage groupings*; Pico de Orizaba: *low Ce, Fe, La, and Zn*; ranging to low Ba and Th; ranging to high Ta; *Cs values between debitage groupings*; Tulancingo: *high Ce, Fe, La, Ta, and Zn*; ranging to low Ba, Mn, and U; ranging to high Na; *Cs values between debitage groupings*; Ucareo: *low Ba and Mn*; *high Ce*; ranging to low Fe; ranging to high La; Zacuáltipan: *low Ba and Mn*; *high Ce, Cs, La, Rb, Ta, Th, and U*; ranging to high K; Zaragoza: *low Ba and Mn*; *high Ce, La, and Th*; ranging to high K, Ta, and U; *Cs values between debitage groupings*; Zinapécuaro: *low Ba, La, and Mn*; *high Th*; ranging to low Ce and Fe; ranging to high Cs, Rb, Ta, and U.

Table D-1. Obsidian Source Data (in ppm) Utilized in This Study.

Country and Obsidian Source Name	Aluminum (Al) Values	Barium (Ba) Values	Calcium (Ca) Values	Cerium (Ce) Values
EL SALVADOR				
Santa Ana Volcano	n/a	650	6000	n/a
GUATEMALA				
Cruz de Apan	n/a	1124 - 1153	n/a	n/a
El Chayal	n/a	866.0 - 924.5	n/a	43.8988 - 46.9870
Ixtepeque	n/a	1016.5 - 1045.3	n/a	40.1026 - 41.9406
Jalapa	n/a	743 - 787	n/a	50.6 - 52.2
Laguna de Ayarza/Media Cuesta [a]	n/a	879 - 943	n/a	46.4 - 48.9
Palo Gordo	n/a	1190 - 1380	n/a	43.8 - 47.4
San Bartolomé Milpas Atlas	n/a	1050 - 1110	n/a	39.3 - 42.8
San Lorenzo	n/a	1070 - 1170	n/a	35.7 - 36.6
San Martín Jilotepeque	n/a	1019.0 - 1072.1	n/a	44.4630 - 49.3220
Sansare	n/a	681 - 717	n/a	46.2 - 51.9
HONDURAS				
Agua Helada	n/a	182 - 196	n/a	52.2 - 73.0
Agua Sucia	n/a	573 - 689	n/a	58.8 - 64.8
El Paraiso	n/a	658	n/a	81.9
Güinope	67000 - 70400	952.3 - 1114	n/a	47.6701 - 51.6
La Esperanza	n/a	735.7 - 798.4	n/a	46.9020 - 49.5690
San Luis	n/a	312 - 462	n/a	56.3 - 58.3
NICARAGUA				
El Horno [b]	--	--	--	--
Lake Nicaragua	60800 - 66600	1584 - 1920	n/a	25.55 - 40.4
Luisitio	n/a	1185 - 1294	~50000 - 70000	~30
MEXICO [c]				
Altotonga	n/a	87 - 101	n/a	75.3 - 77.3
Guadalupe Victoria	n/a	855.8 - 1220	n/a	23.54 - 29.14
Otumba	n/a	664.7 - 786	n/a	48.94 - 52.8
Pachuca	n/a	7 - 51.8	n/a	88.3 - 150.64
Paredón	n/a	49.4 - 82	n/a	105.23 - 112
Pico de Orizaba	n/a	683 - 1020	n/a	12.9 - 16.7
Tulancingo	n/a	636 - 816	n/a	137.7 - 172
Ucareo	n/a	119 - 179.8	n/a	62.53 - 69.47
Zacuáltipan	n/a	238 - 296.2	n/a	106 - 110
Zaragoza	n/a	417.57 - 468	n/a	71.66 - 74.5
Zinapécuaro	n/a	326 - 519	n/a	27.8 - 48.2

[a] All Laguna de Ayarza and Media Cuesta data compared had already been pre-grouped; see text.

[b] There are no known chemical data (or collected specimens) for the "El Horno" source; see text.

[c] Only 11 (of the 66 total known) Mexican obsidian sources were compared in this study; see text.

The chemical data in this table were compiled from the following sources: Aoyama et al. 1999; Braswell 1996; Carballo et al. 2007; Cobean et al. 1991; Michael Glascock, written communication 4/22/1997; Glascock et al. 1988; Nelson et al. 1983; Sheets et al. 1990; Stross et al. 1976; Stross et al. 1992; Vogt et al. 1982. See text for further details.

Table D-1 (continued). Obsidian Source Data (in ppm) Utilized in This Study.

Country and Obsidian Source Name	Cesium (Cs) Values	Iron (Fe) Values	Potassium (K) Values
EL SALVADOR			
Santa Ana Volcano	n/a	10000	27000
GUATEMALA			
Cruz de Apan	n/a	12555 - 12904	n/a
El Chayal	7.2109 - 7.5480	5825.6 - 6104.2	30112.0 - 36405.4
Ixtepeque	2.5060 - 2.5850	8760.2 - 8945.0	33280.0 - 35040.0
Jalapa	7.92 - 8.22	7930 - 8210	32000 - 38700
Laguna de Ayarza/Media Cuesta [a]	2.83 - 3.00	8470 - 9990	29200 - 38900
Palo Gordo	5.04 - 5.61	10000 - 11300	30100 - 32900
San Bartolomé Milpas Atlas	3.22 - 3.39	7750 - 8300	31700 - 41800
San Lorenzo	3.96 - 4.53	6520 - 7160	31500
San Martín Jilotepeque	3.0920 - 3.2311	5996.6 - 6541.4	28789.5 - 35687.9
Sansare	6.45 - 6.82	12120 - 13000	31600 - 37200
HONDURAS			
Agua Helada	3.36 - 3.44	6300 - 6380	41000 - 44200
Agua Sucia	2.5 - 2.7	7510 - 8390	36900 - 42900
El Paraiso	2.75	13000	46900
Güinope	7.5610 - 7.98	8361.6 - 8880	33870.0 - 43400
La Esperanza	4.2140 - 4.5220	7953.8 - 8672.4	33590.0 - 40020.0
San Luis	3.09 - 3.23	7160 - 7860	40700 - 42700
NICARAGUA			
El Horno [b]	--	--	--
Lake Nicaragua	1.69 - 2.46	10680 - 11880	22100 - 33000
Luisitio	n/a	~65000 - 85000	n/a
MEXICO [c]			
Altotonga	4.48 - 4.58	7820 - 8040	38700 - 41900
Guadalupe Victoria	3.28 - 3.96	4190 - 4510	29800 - 36400
Otumba	3.60 - 4.00	7447.5 - 8814.5	30400 - 35932
Pachuca	1.97 - 4.41	13703 - 17089	34174 - 43416
Paredón	5.32 - 5.69	8066 - 9014	38719 - 42744
Pico de Orizaba	3.92 - 4.22	3440 - 4000	32000 - 36900
Tulancingo	5.23 - 6.5	16709 - 18700	30014 - 40300
Ucareo	6.66 - 7.4	6964 - 7573	37478 - 40968
Zacuáltipan	15.3 - 16.4	10089 - 11100	40400 - 46800
Zaragoza	3.92 - 4.23	8857 - 9530	38357 - 43300
Zinapécuaro	8.7 - 14.5	6370 - 7180	34600 - 36600

[a] All Laguna de Ayarza and Media Cuesta data compared had already been pre-grouped; see text.

[b] There are no known chemical data (or collected specimens) for the "El Horno" source; see text.

[c] Only 11 (of the 66 total known) Mexican obsidian sources were compared in this study; see text.

The chemical data in this table were compiled from the following sources: Aoyama et al. 1999; Braswell 1996; Carballo et al. 2007; Cobean et al. 1991; Michael Glascock, written communication 4/22/1997; Glascock et al. 1988; Nelson et al. 1983; Sheets et al. 1990; Stross et al. 1976; Stross et al. 1992; Vogt et al. 1982. See text for further details.

Table D-1 (continued). Obsidian Source Data (in ppm) Utilized in This Study.

Country and Obsidian Source Name	Lanthanum (La) Values	Manganese (Mn) Values	Sodium (Na) Values
EL SALVADOR			
Santa Ana Volcano	n/a	400	n/a
GUATEMALA			
Cruz de Apan	n/a	720 - 767	16692 - 16914
El Chayal	23.6765 - 26.1181	627.15 - 678.28	29837.1 - 31740.0
Ixtepeque	22.8251 - 23.3712	441.35 - 471.63	28660.0 - 30400.0
Jalapa	26.5 - 27.7	505 - 533	26300 - 27900
Laguna de Ayarza/Media Cuesta [a]	23.2 - 24.9	834 - 1022	32400 - 37200
Palo Gordo	25.1 - 27.7	637 - 669	32600 - 34600
San Bartolomé Milpas Atlas	21.9 - 22.6	513 - 526	30000 - 31000
San Lorenzo	21.3 - 24.6	427	28000 - 31000
San Martín Jilotepeque	24.8800 - 27.5700	490.57 - 552.31	26350.0 - 29330.6
Sansare	24.8 - 27.4	585 - 640	28300 - 31000
HONDURAS			
Agua Helada	29.5 - 39.1	358 - 362	25600 - 28200
Agua Sucia	31.1 - 33.3	668 - 726	31100 - 31900
El Paraiso	138	312	19500
Güinope	27.3150 - 28.9	498.72 - 529	25260.0 - 27500
La Esperanza	26.9700 - 27.5100	400.20 - 454.43	25380.0 - 28614.7
San Luis	31.2 - 32.4	368 - 376	27900 - 28700
NICARAGUA			
El Horno [b]	--	--	--
Lake Nicaragua	11.8 - 17.7	599 - 653	31000 - 33300
Luisitio	n/a	n/a	n/a
MEXICO [c]			
Altotonga	39.7 - 40.5	229 - 247	27400 - 29000
Guadalupe Victoria	10.64 - 19.6	502 - 533.76	30229 - 38900
Otumba	23.88 - 27.5	345.3 - 395.7	28674 - 31875
Pachuca	36.8 - 65.24	773.5 - 1229	34977 - 39380
Paredón	48.19 - 54.46	336.75 - 366.82	27336 - 29659
Pico de Orizaba	5.6 - 8.73	507 - 574	29800 - 36000
Tulancingo	66.94 - 83.4	345.6 - 453	30177 - 38500
Ucareo	31.7 - 35.75	163 - 170.33	27244 - 28140
Zacuáltipan	51.0 - 53.6	155 - 180	23100 - 25200
Zaragoza	35.76 - 38.64	234 - 254	28100 - 29900
Zinapécuaro	11.4 - 23.4	175 - 225	27500 - 30500

[a] All Laguna de Ayarza and Media Cuesta data compared had already been pre-grouped; see text.

[b] There are no known chemical data (or collected specimens) for the "El Horno" source; see text.

[c] Only 11 (of the 66 total known) Mexican obsidian sources were compared in this study; see text.

The chemical data in this table were compiled from the following sources: Aoyama et al. 1999; Braswell 1996; Carballo et al. 2007; Cobean et al. 1991; Michael Glascock, written communication 4/22/1997; Glascock et al. 1988; Nelson et al. 1983; Sheets et al. 1990; Stross et al. 1976; Stross et al. 1992; Vogt et al. 1982. See text for further details.

Table D-1 (continued). Obsidian Source Data (in ppm) Utilized in This Study.

Country and Obsidian Source Name	Rubidium (Rb) Values	Strontium (Sr) Values	Tantalum (Ta) Values
EL SALVADOR			
Santa Ana Volcano	140	135	n/a
GUATEMALA			
Cruz de Apan	77 - 80	314 - 343	n/a
El Chayal	133.55 - 142.60	119.86 - 174.87	0.9391 - 0.9848
Ixtepeque	91.22 - 96.04	146.72 - 163.73	0.7564 - 0.7958
Jalapa	148 - 151	169 - 198	0.924 - 0.959
Laguna de Ayarza/Media Cuesta [a]	100 - 110	98 - 243	0.758 - 0.829
Palo Gordo	93.1 - 102	n/a	0.575 - 0.910
San Bartolomé Milpas Atlas	118 - 126	126 - 148	0.597 - 0.628
San Lorenzo	98.7 - 103	n/a	0.587 - 0.922
San Martín Jilotepeque	104.70 - 111.00	164.89 - 221.90	0.7610 - 0.8070
Sansare	134 - 145	246 - 281	0.922 - 0.995
HONDURAS			
Agua Helada	143 - 147	14.1 - 24.7	1.44 - 1.48
Agua Sucia	104 - 112	58.1 - 111.1	1.53 - 1.63
El Paraiso	129	201	1.5
Güinope	141 - 181	167.14 - 179.49	0.8747 - 0.9122
La Esperanza	140.60 - 147.90	133.55 - 164.68	0.9444 - 0.9850
San Luis	135 - 139	30.6 - 74.0	1.33 - 1.39
NICARAGUA			
El Horno [b]	--	--	--
Lake Nicaragua	60.2 - 70.3	n/a	0.265 - 0.283
Luisitio	n/a	n/a	n/a
MEXICO [c]			
Altotonga	143 - 147	n/a	1.66 - 1.70
Guadalupe Victoria	83.0 - 113.4	n/a	0.67 - 1.32
Otumba	113 - 131.01	n/a	0.97 - 1.12
Pachuca	115.36 - 223.7	n/a	3.07 - 4.97
Paredón	157.1 - 173.6	n/a	2.48 - 3.04
Pico de Orizaba	98 - 108	n/a	0.866 - 1.57
Tulancingo	115.78 - 138	n/a	1.86 - 2.45
Ucareo	140.2 - 158	n/a	1.16 - 1.24
Zacuáltipan	274 - 308	n/a	1.7 - 1.96
Zaragoza	130.42 - 145.46	n/a	1.36 - 1.53
Zinapécuaro	166 - 267	n/a	1.36 - 5.06

[a] All Laguna de Ayarza and Media Cuesta data compared had already been pre-grouped; see text.

[b] There are no known chemical data (or collected specimens) for the "El Horno" source; see text.

[c] Only 11 (of the 66 total known) Mexican obsidian sources were compared in this study; see text.

The chemical data in this table were compiled from the following sources: Aoyama et al. 1999; Braswell 1996; Carballo et al. 2007; Cobean et al. 1991; Michael Glascock, written communication 4/22/1997; Glascock et al. 1988; Nelson et al. 1983; Sheets et al. 1990; Stross et al. 1976; Stross et al. 1992; Vogt et al. 1982. See text for further details.

Table D-1 (continued). Obsidian Source Data (in ppm) Utilized in This Study.

Country and Obsidian Source Name	Thorium (Th) Values	Uranium (U) Values	Zinc (Zn) Values
EL SALVADOR			
Santa Ana Volcano	n/a	n/a	n/a
GUATEMALA			
Cruz de Apan	n/a	n/a	n/a
El Chayal	9.4320 - 9.9233	4.8165 - 5.4443	30.58 - 36.85
Ixtepeque	6.3360 - 6.5740	2.2280 - 2.4070	28.36 - 29.74
Jalapa	10.58 - 10.8	3.71 - 4.49	35.0 - 38.9
Laguna de Ayarza/Media Cuesta [a]	6.83 - 7.20	2.43 - 3.12	38.9 - 50.3
Palo Gordo	10.0 - 10.9	3.64 - 3.97	45.6 - 51.7
San Bartolomé Milpas Atlas	8.65 - 9.24	2.85 - 3.29	32.4 - 35.8
San Lorenzo	9.50 - 9.76	3.67 - 4.06	29.4 - 34.7
San Martín Jilotepeque	8.1030 - 8.5170	2.5240 - 3.2660	29.43 - 33.93
Sansare	10.10 - 11.06	4.14 - 4.65	38.2 - 47.1
HONDURAS			
Agua Helada	14.4 - 14.6	4.44 - 4.74	29.8 - 30.2
Agua Sucia	10.1 - 10.9	4.11 - 4.63	46.6 - 52.4
El Paraiso	10.6	3.72	44
Güinope	11.0190 - 12.19	3.89 - 4.5340	35.93 - 37.39
La Esperanza	10.4450 - 11.0590	3.5610 - 4.0600	32.53 - 34.72
San Luis	13.1 - 13.7	4.38 - 4.72	31.0 - 32.2
NICARAGUA			
El Horno [b]	--	--	--
Lake Nicaragua	3.10 - 3.54	1.35 - 1.52	n/a
Luisitio	n/a	n/a	n/a
MEXICO [c]			
Altotonga	21.0 - 21.4	5.30 - 6.14	37.1 - 38.3
Guadalupe Victoria	7.21 - 8.19	4.16 - 5.53	24.2 - 48.4
Otumba	9.72 - 10.68	2.83 - 3.76	38.83 - 44.91
Pachuca	10.69 - 20.90	3.25 - 9.00	116.33 - 284.1
Paredón	14.81 - 17.2	4.19 - 5.96	48.27 - 65.73
Pico de Orizaba	6.02 - 6.95	4.58 - 5.43	21.8 - 27.6
Tulancingo	9.73 - 13.9	1.55 - 4.2	166 - 244.3
Ucareo	13.56 - 14.2	3.82 - 4.8	32.84 - 40
Zacuáltipan	35.2 - 36.5	9.72 - 11.9	33.56 - 42.44
Zaragoza	18.75 - 19.45	5.04 - 5.96	37.5 - 45.34
Zinapécuaro	15.3 - 22.2	5.14 - 7.95	34.3 - 58.3

[a] All Laguna de Ayarza and Media Cuesta data compared had already been pre-grouped; see text.

[b] There are no known chemical data (or collected specimens) for the "El Horno" source; see text.

[c] Only 11 (of the 66 total known) Mexican obsidian sources were compared in this study; see text.

The chemical data in this table were compiled from the following sources: Aoyama et al. 1999; Braswell 1996; Carballo et al. 2007; Cobean et al. 1991; Michael Glascock, written communication 4/22/1997; Glascock et al. 1988; Nelson et al. 1983; Sheets et al. 1990; Stross et al. 1976; Stross et al. 1992; Vogt et al. 1982. See text for further details.