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HANDHELD XRF ANALYSIS OF YUGÜE OBSIDIAN

by

JESSICA L. CLARK

A thesis submitted in partial fulfillment of the requirements for the Honors in the Major Program in Anthropology in the College of Sciences and in the Burnett Honors College at the University of Central Florida Orlando, Florida

Spring Term

2021

Thesis Chair: Brigitte Kovacevich, PhD

ABSTRACT

Analysis was performed on a 31-artifact sample of Late Terminal Formative obsidian excavated in 2003 from the archaeological site of Yugüe in the Lower Verde Valley of Oaxaca. This analysis was performed to determine the geochemical sources of the individual obsidian artifacts and replicate a prior study of Yugüe obsidian performed by David T. Williams for his thesis at the University of Colorado. This earlier analysis determined that five obsidian sources were present. Sourcing was accomplished using a handheld X-Ray fluorescence instrument and bivariate plotting of relevant trace elements. Five sources of obsidian were found during analysis: Pachuca, Otumba, Paredon, Guadalupe Victoria, and Zaragoza. Williams identified additional sources that were not identified in this study, but he also may have sampled artifacts from the site from other excavations. This previous analysis by Williams also did not attribute sources to individual artifacts, making it impossible for archaeological conclusions to be drawn about the life histories of particular artifacts. By attributing sources to individual artifacts during analysis, this project provides valuable context about both the site of Yugüe during the Terminal Formative period and the lower Rio Verde Valley.

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INTRODUCTION

Compositional analysis of obsidian using handheld XRF was undertaken in this project to determine the number of obsidian sources represented in a Terminal Formative sample from the site of Yugüe. A previous analysis of Terminal Formative obsidian artifacts by Williams found five sources of obsidian present during the period and additional changes to sources after the Terminal Formative at Yugüe. This project aimed to determine which sources could be attributed to the sampled artifacts from Yugüe and examine the distribution of sources across artifacts. The relative political centralization of the Rio Verde valley in the Terminal Formative period was expected to be reflected in an even distribution of obsidian sources at the site, with relatively equal numbers of obsidian material attributed to each source.

Geography and Time

The Terminal Formative period in Oaxaca, between 150 BCE and 250 CE, was characterized by the apogee of a trend of political centralization that began in the Middle Formative period, which occurred in 700-400 BCE (Joyce, 2008, pp.223-224). 250 CE marks a political collapse that was not overcome until the start of the Late Classic period 250 years later (Joyce, 2008, p.221). A potential cause of this collapse was the contentious relationship between different systems of authority in the region: traditional egalitarianism and rising centralized inequality (Joyce, 2008, p.229).

Over the Terminal Formative period, social complexity, social inequality, population, and communal practices, such as monumental construction and ritual feasting, increased dramatically. Luxury goods are also markers of social inequality in the region, as they were

acquired and traded by nobles (Joyce, 2008, p.225). These goods became more and more available to elites during this time, as trade networks were expanding across Mesoamerica. However, Joyce (2008, pp.227-228) argues that, at this period, these items were often used to increase community status rather than the status of individuals, as prestige goods were often cached in communal, monumental structures; although political centralization did occur, aggrandizement of individual elite or nobles was not prevalent. Having obsidian from multiple sources at a site indicates the presence of complex and often far-flung trading networks.

The Rio Verde Valley of Oaxaca developed a three-tiered settlement hierarchy, with a capital city at Rio Viejo. The tertiary site of Yugüe was 10 hectares compared to Rio Viejo's 225 but still had significant social complexity, indicated by monumental construction and burials of differential status (Joyce, 2008, p.223-225). Yugüe was close to other tertiary and secondary sites and was only 4 kilometers away from Rio Viejo. Yugüe was occupied between the late Middle Formative to the Late Terminal Formative (Barber, 2005, pp.129-130).

Obsidian

Because of obsidian's nature as a volcanic mineral, it is restricted in source to sites with lava flows. These sources determine specific chemical compositions of obsidians based on trace elements (Liritzis & Zacharias, 2011, p.126). Thus, by analyzing a unique obsidian composition, it is possible to determine exactly where the obsidian originated through comparison to analyses of potential sources. Because of the ubiquity of obsidian in Mesoamerica and its limited number of sources, obsidian analysis is a very useful tool for studying economic and political exchange across space (Joyce et al., 1995, p.4).

X-Ray Fluorescence

X-Ray Fluorescence (XRF) is a highly useful technique for sourcing archaeological materials, such as obsidian and ceramics. Handheld XRF models have become highly popular in archaeology, as they are cost-effective, powerful, and easily moved and used in the field. Portable, handheld models are not quite as powerful as stationary models, however, and their accuracy has not been sufficiently tested and compared to stationary models (Shackley, 2010, p.18). Handheld XRF is a very exciting technology with much promise but has significant limitations.

XRF is the process in which a photon is emitted from an x-ray source toward a given sample, which then displaces an electron from the inner shell of an atom. This causes an electron from a higher energy shell to fill the void left by the absence of the lower energy inner electron. By dropping to a lower energy shell, a specific quantity of energy, determined by the positive attraction exerted on electrons by the number of protons in an atom's nucleus, is displaced. This energy displacement is detected and measured by the XRF to determine the atomic identity of a sample (Drake, 2014).

Handheld X-Ray Fluorescence

Handheld XRF (hXRF), also known as portable XRF, or PXRF, is a type of noninvasive, rapid, and effective detector that is compact, low weight, requires less power than regular XRF, and can use varying voltages and currents (Liritzis & Zacharias, 2011, p.109). Handheld XRF devices are cost-effective, are highly sensitive, have powerful built-in analytic engines, and can be automated and worked remotely (Liritzis & Zacharias, 2011, p.110).

There are certain limitations of hXRF that affect data collection and analysis. Sample thickness affects the elemental precision of sampling (Liritzis & Zacharias, 2011, pp.127-128). Samples must have the appropriate thickness to study particular target elements, and if they don't, accuracy may be impacted. The sample being studying should be flat for optimal reading, or else the surface roughness "introduces an additional air gap between sample and PXRF analyzer" (Liritzis & Zacharias, 2011, p.132). Concentrations near the detection limit threshold are suspect and should be disregarded in analysis. Conversion from X-ray to concentration data is imperfect and introduces error (Liritzis & Zacharias, 2011, pp. 134-135). Standards for hXRF are also not clearly established in archaeology. Reliability and validity, defined by Shackley (2010, p.18) as replication of results and testing the data by other means, respectively, are not tested often and consistently by hXRF users, making it difficult to test and compare their accuracy. Very few standards have been established for the use of hXRF or how different hXRF models should be calibrated to test the same samples (Shackley, 2010, p.19).

There are a plethora of advantages to hXRF that make it very useful for archaeologists. It is non-invasive and non-destructive, which is important for conservation and preservation, and allows for sourcing to take place on historical and archaeological materials that are precious and irreplaceable. The hXRF devices are highly portable, allowing them to be used much more easily in the field and in museums than larger benchtop models, and process results quickly and effectively, with "satisfactory" accuracy and precision (Liritzis & Zacharias, 2011, p.135). Handheld XRF models are also much cheaper and easier to use than wavelength XRF models (Shackley, 2010, p.18).

Altogether, hXRF is an incredibly useful technology that can provide a wealth of knowledge to archaeologists both in the field and in labs for relatively low costs. For all its accessibility and power, each individual model must be analyzed and calibrated to ensure precision and accuracy, and samples must be prepared with care so that extra error is not introduced during analysis. Handheld XRF is not a perfect technology, but it has exciting prospects for sourcing and archaeological analysis.

Obsidian Analysis

According to Ferguson (2012, p.401), using handheld XRF for obsidian provenance requires "an understanding of X-Ray physics, igneous petrology, the calibration process, and the ability to test a sufficient variety of homogenous and well-characterized reference materials suitable for developing a valid calibration curve." This extensive list is emblematic of the complexity of handheld XRF, which has been misrepresented by some archaeologists as only needing to be pointed and shot at samples for accurate analysis.

For a material to be accurately provenanced, it must exhibit more variability between sources than within them. As obsidian has uniform chemistry within its limited sources, it is a perfect candidate for provenance (Ferguson, 2012, pp.401-402). To accurately provenance obsidian with XRF, samples and data from different potential obsidian sources need to be gathered and analyzed, preferably with the same device used on the obsidian to be sourced so as to not introduce error from different calibration methods and standards (Shugar & Mass, 2012, p.27). The ranges of concentrations of the elements to be studied should be greater in the reference samples than what is expected to be found in the obsidian to be studied (Shugar & Mass, 2012, p.27).

For XRF analysis to be as accurate as possible, the fluorescence of the elements being analyzed should be maximized so that those elements are best detected. To maximize fluorescence, the energies of the X-Rays should be just above the excitation energies of the element being studied in the sample (Ferguson, 2012, p.412). XRF is a surface analysis technique, which makes it difficult to use for the analysis of heterogeneous or layered materials. While obsidian is a fairly homogenous material, if a sample had a substantial patina or thin covering of non-characteristic material, it could skew the analysis (Shugar & Mass, 2012, p.18).

XRF samples should be infinitely thick, that is having, "the thickness at which additional sample thickness does not result in additional fluorescent X-rays," as specified by the elements being analyzed (Ferguson, 2012, p.413). Every element has a different infinite thickness, making analysis for multiple elements with one sample difficult. If a sample is less than the infinite thickness of an element in question, a researcher must normalize the data using corrections derived from the rhodium Compton peak area. The Compton peak represents the inelastic scatter produced in the X-Ray fluorescence process and is a direct reflection of the mass of the sample being studied. By ratioing smaller flakes and debitage to their Compton scatter peaks, their composition is normalized and gives the same elemental compositions of the larger pieces they were struck from (Shackley, 2011, p.23). This normalization can correct high energy element fluctuations but tends to overcorrect for low energy elements such as iron, making it more useful for high energy elements (Ferguson, 2012, pp.414-416).

Calibration is of the utmost importance. There are no universally accepted standards for XRF calibration. Most of the available standards are powdered, which can introduce 5 to 25% error when used to develop calibrations for solid samples (Ferguson, 2012, pp.408-409). A

common standard for obsidian may not even be practical, as obsidian composition is too varied to lend itself easily to not use specific calibrations for individual sample matrices (Ferguson, 2012, p.409). There is controversy over whether precision and accuracy or consistent separation of sources are more important when sourcing obsidian. Accuracy and precision, from Shackley's (2011) definitions, are how closely a sample's measured value matches its true value (p.208) and the capability of an instrument of consistently measuring the same results from the same sample (p.220). While ideally, none should be sacrificed, and an effective analysis relies on all of those factors, Ferguson (2012, p.410) argues that the identification of sources is more important than extreme precision and replicability across all labs and instruments.

Data Sources

The obsidian artifacts under analysis derive from excavations at the site of Yugüe as a component of Proyecto Rio Verde 2003, which aimed to study the development of statehood and organization in the lower Rio Verde valley over the Terminal Formative period (Barber, 2004, pp.2-4). The obsidian material consists of 31 artifacts, identified as flakes, prismatic blades, and pieces of debitage by Williams (2012, pp.61). Artifacts shall be referred to by their FS numbers assigned to them during excavation and by additional numbers if multiple artifacts belong to the same FS number. All artifacts are from Operation 1 except for 158, 960, 941, and 1802, which are from Operation 2. 15 artifacts, 1000_1 to 1000_15, actually date to the Late Postclassic, and are separated in the analysis (S. Barber, personal communication, December 17, 2020).

METHODOLOGY

Instrumentation

X-ray Fluorescence (XRF) was chosen to analyze obsidian due to the process being fast, non-destructive, cost-effective, and requiring only minimal preparation. XRF instruments can perform compositional analysis in seconds and do not cause any harm to samples. Due to the speed of analysis, cost-per-sample analysis is reduced. Analysis can take place without samples needing to be treated or intensively cleaned due to XRF's reaching below the surface of artifacts being analyzed (Shackley, 2011, pp.8-9).

An hXRF instrument, the Bruker Tracer III-SD model, was used to analyze chemical compositions. Portable instruments allow for analysis to take place both inside and out of the lab and are more affordable than stationary devices while remaining both powerful and accurate (Shackley, 2011, p.10).

XRF is not a perfect process. Samples are restricted in size to being over 10 mm in their smallest dimension and at least 2 mm thick (Shackley, 2011, pp.9-10). However, Frahm (2016, p.463) has found success with sourcing 1 to 2 mm obsidian chips with XRF by utilizing novel data handling protocols. HXRF technology is also not without flaws and produces more errors than XRF instruments that are stationary. Handheld instruments require more calibration than stationary ones in order to minimize errors (Shackley, 2011, p.13). HXRF analysis detects fewer elements than stationary fluorescence, only up to atomic number 51, due to decreased power from the limits of portable battery capacity (Shackley, 2010, p.17). However, Migliori et al.

(2011, p.111) have successfully identified elements with lower atomic numbers than can typically be found with standard XRF practices by utilizing helium flow.

Standards for hXRF analysis have not been universally established. Publications frequently do not include information on instrumentation settings and calibration, making it difficult to determine the reliability and validity of the technology (Shackley, 2010, p.19). Reliability and validity, defined by Shackley (2010, p.18), are the replication of results and the testing data by other means, respectively.

hXRF Process

Each sample was weighed before analysis. Each sample was exposed to the X-ray beam for 180 seconds, following Williams' methodology (Williams, 2012, p.43). A 25-ampere anode current was used to generate 40 keV X-rays. A green filter, consisting of 12 parts per million of Aluminum, 1 part Titanium, and 6 parts Copper, was used for the hXRF instrument, filtering out non-relevant elements and optimizing for relevant heavier elements such as rubidium, strontium, yttrium, and zirconium (Drake, 2018).

Trace elements are identified through XRF using the reactions of atoms to X-ray radiation; the energy from the X-ray separates an inner shell electron from the atom and causes a release of energy to be emitted. This energy, fluorescent radiation, is equal to the energy difference between the electron shells of the particular elements composing the sample under study (Shackley, 2011, p.16).

Obsidian is a homogenous, glassy material with high silica content. Obsidian is generally composed of "about 66-75% SiO2, 10-15% Al2O3, 3-5% Na2O, 2-5% K2O, and 1-5% total

Fe2O3 + FeO," with other elements occurring at concentrations less than 1% (Glascock, 2002, pp.611-612). Each obsidian source has a homogeneous chemical composition that differs from other sources, particularly in the concentrations of trace elements (Glascock, 2002, p.612). The chemical composition of obsidian artifacts can therefore be compared to the composition of potential volcanic sources to determine where they originated. Williams paid particular attention to the trace elements potassium, titanium, manganese, iron, zinc, gallium, rubidium, strontium, yttrium, zirconium, niobium, thorium, and lead (2012, p.607). Ferguson (2012, p.408) suggests that of these elements, iron, rubidium, strontium, yttrium, zirconium, and niobium are the most relevant in identification. Following both Ferguson's suggestions and the methods outlined by Williams, this analysis focused primarily on iron, rubidium, strontium, yttrium, zirconium, zinc, and manganese, as these appeared to create the best groupings of artifacts with source samples.

Williams compared the compositions of the artifacts studied with the compositions of the Mesoamerican sources of El Chayal, Ixtepeque, San Martin Jilotepeque, Guadalupe Victoria, Pico de Orizaba, Otumba, Paredón, Pachuca, Ucareo, Zaragoza, and Zacualtipan (Williams, 2012, p.44). These sources are plotted on a map of Mesoamerica in Figure 1. Williams (2012, p.98) determined that obsidian from five sources were present at the site in the Late Terminal Formative period: Zaragoza, Otumba, Guadalupe Victoria, Pachuca, and Ucareo. This analysis compared the artifact compositions to those of El Chayal, Ixtepeque, Otumba, Paredon, Pachuca, San Martin Jilotepeque, Tulancingo, Ucareo, Zacualtipan, Cerro Veral, Zaragoza, Altotonga, Guadalupe Victoria, and Pico de Orizaba. These sources were those made available over the course of the project by the University of Missouri Research Reactor Center (MURR) and were shot in using the UCF Bruker Tracer III-SD.



Figure 1: Map of Mesoamerican Obsidian Sources Used by Williams

Adapted from: Glascock, 2002.

Calibration

The spectrum files were run through a calibration for the specific instrument provided by the manufacturer, Bruker, based on the MURR calibration for Mesoamerican Obsidian. A standard sample prepared from rhyolite from the United States Geological Survey, RGM-2, was also read with the instrument to ensure effective calibration. This calibration transformed the elemental data from photon counts to parts per million.

Statistical Analysis

The Bruker was set to use a voltage of 40 kV and 25 µA current for 180 seconds, following Waite's (2020, p.45) methodology, as Williams did not specify the voltage and current used over the course of analysis. Several pieces, 447, 1502_2, and 1720, were small enough that there was a question of them not completely covering the hXRF aperture, which could have skewed the analysis. However, these pieces did not show as outliers over the course of analysis and thus can be assumed to have been scanned in relatively accurately during the fluorescence process.

The SAS JMP Pro 12 program was used to construct bivariate plots comparing elemental compositions, which were then used to assign artifacts to sources. Williams used biplots comparing the elements Sr to Y, Rb to Zr, Rb to Sr, and Rb to Ba (2012, pp.96-100). But aside from including some bivariate plots attributed to Glascock, he does not describe how sources were attributed to samples. Waite, in her analysis of obsidian from the sites of Coba and Yaxuna, utilized the Sr, Zr, and Rb to create biplots (2020, p.50). All available sources were plotted on bivariate charts comparing concentrations of the elements Mn, Fe, Zn, Rb, Sr, Y, Zr to each other. Bivariate element plots were used to identify sources, as each source clusters distinctively in particular elemental comparisons. The biplots that most effectively and repeatedly grouped the artifacts with source samples are presented here (see below).

Artifacts were plotted alongside the sources, and artifacts clustering with individual sources were attributed to those sources. Sources with no artifacts attributed to them were systematically removed. Each elemental biplot was examined, and 95% confidence density ellipses were applied to each cluster in order to determine their accuracy.

RESULTS

The results of this analysis suggest that people at Yugüe utilized multiple obsidian sources during the Late Terminal Formative period and only two during the Late Postclassic. More obsidian sources were found during the analysis of artifacts from Operation 1 than from Operation 2, although this could be attributed to the greater number of artifacts from Operation 1 represented in this sample.

Table 1

Late Terminal Formative Source Attributions Statistics

Source	Number of Artifacts	Percentage of Total
Pachuca	6	37.5
Zaragoza	5	31.25
Paredon	2	12.5
Guadalupe Victoria	2	12.5
Otumba	1	6.25
Total	16	100

Table 2

Late Postclassic Source Attributions Statistics

Source	Number of Artifacts	Percentage of Total
Pachuca	14	93
Paredon	1	7
Total	15	100

Table 1 describes the distribution of sources among the 16 Late Terminal Formative analyzed artifacts. 6 of the artifacts were from Pachuca, and five of the artifacts were determined to be from Zaragoza. Two of the artifacts were determined to be from Paredon, and another two of the artifacts were from Guadalupe Victoria. The last artifact was determined to be from Otumba, Mexico.

Table 2 represents the artifact distribution from the 15 artifacts from a Late Postclassic feature. 14 artifacts were found to be from Pachuca, and only one was found from Paredon.

Operation 1 of the 2003 excavation produced artifacts from each source, while Operation 2 produced artifacts from only Pachuca and Zaragoza. Figure 2 is a map of Mesoamerica where the sources found by the author and Williams are plotted. The source attributions for the Late Terminal Formative artifacts are represented in Table 3, and the Postclassic artifacts in Table 4.



Figure 2: Map of Mesoamerican Obsidian Sources Found at Yugüe

Adapted from: Glascock, 2002; Barber, 2005.

Table 3

FS#	Operation	Unit	Lot	Weight (g)	Form	Source
0070_1	1	0G222	2	0.7	Blade	Pachuca, Hidalgo
0070_2	1	0G222	2	0.2	Blade	Pachuca, Hidalgo
0158_1	2	MU4	1	1.1	Blade	Pachuca, Hidalgo
0447_1	1	2G219	2	0.1	Flake fragment	Zaragoza, Puebla
0463_1	1	7H224	4	0.6	Flake fragment	Paredon, Puebla
0592_1	1	0G221	3	0.4	Chunk	Zaragoza, Puebla
0728_1	1	1I226	2	2.2	Chunk	Zaragoza, Puebla
0941_1	2	8N53	2	0.5	Blade	Zaragoza, Puebla
0960_1	2	4051	3	1.1	Flake	Zaragoza, Puebla
1282_1	1	8H227	3	0.4	Flake	Guadalupe Victoria, Puebla
1502_1	1	1G225	4	0.6	Blade	Pachuca, Hidalgo
1502_2	1	1G225	4	0.1	Flake fragment	Pachuca, Hidalgo
1502_3	1	1G225	4	1.2	Flake	Paredon, Puebla
1633_1	1	9H229	5	0.2	Blade	Pachuca, Hidalgo
1720_1	1	3I225	3	0.2	Flake	Guadalupe Victoria, Puebla
1801_1	1	3050	2	0.3	Flake	Otumba, Mexico

Late Terminal Formative Artifact Source Attributions

Source: Williams, 2012, pp.551-560.

Table 4

Late Postclassic Artifact Source Attributions

FS#	Operation	Unit	Lot	Weight (g)	Form	Source
1000_01	1	1G225	2	0.6	Blade	Pachuca, Hidalgo
1000_02	1	1G225	2	0.4	Blade	Pachuca, Hidalgo
1000_03	1	1G225	2	0.3	Blade	Pachuca, Hidalgo
1000_04	1	1G225	2	0.6	Blade	Pachuca, Hidalgo
1000_05	1	1G225	2	1.2	Blade	Pachuca, Hidalgo
1000_06	1	1G225	2	1.6	Blade	Pachuca, Hidalgo
1000_07	1	1G225	2	0.7	Blade	Pachuca, Hidalgo
1000_08	1	1G225	2	0.3	Blade	Pachuca, Hidalgo
1000_09	1	1G225	2	0.6	Blade	Pachuca, Hidalgo
1000_10	1	1G225	2	1	Blade	Pachuca, Hidalgo
1000_11	1	1G225	2	1	Blade	Pachuca, Hidalgo
1000_12	1	1G225	2	0.3	Flake	Pachuca, Hidalgo
1000_13	1	1G225	2	1.5	Flake	Pachuca, Hidalgo
1000_14	1	1G225	2	1	Flake fragment	Paredon, Puebla
1000_15	1	1G225	2	0.7	Flake	Pachuca, Hidalgo

Source: Williams, 2012, pp.551-560.

The biplots created over the course of statistical analysis are represented in Figures 4-8. Sources are represented by the abbreviations GP, for Guadalupe Victoria, Puebla ; OM, for Otumba, Mexico; PP, for Paredon, Puebla; SHO, for Sierra de Pachuca, Hidalgo; and ZP, for Zaragoza, Puebla. The Pachuca abbreviation has also been written as SH. Hollow shapes on the biplots represent source samples, while solid circles represent artifacts. The Pachuca artifacts were particularly easy to identify, as their chemical signatures were very different from the other sources in most of the bivariate plots. The Zaragoza and Paredon sources tended to cluster closely together, making differentiation more difficult but not impossible.



Figure 3: Bivariate Plot of Mn by Sr

Figure 4 is the biplot comparing Mn to Sr. In this plot, the Guadalupe Victoria, Otumba, and Pachuca source samples and artifacts are easy to differentiate, with significant normal ellipses confirming their clustering. The Paredon samples and artifacts cluster significantly and distinctly from those of Zaragoza, which are more widely spread and have a low significance of clustering, as evidenced by the significance probability of their normal ellipse in this plot.



Figure 4: Bivariate Plot of Mn by Y

Figure 5 is the biplot comparing Mn to Y. In this plot, Pachuca source samples and artifacts are clearly distinct and separate. While the other sources are plotted closer together, they are all clearly clustered separately. The Otumba, Paredon, Pachuca, and Zaragoza clusters are all significant. However, the Guadalupe Victoria source samples are not contained in a significant ellipse.



Figure 5: Bivariate Plot of Rb by Sr

Figure 6 is the biplot comparing Rb to Sr. In this plot, only Paredon and Zaragoza are clustered significantly. While Otumba and Guadalupe Victoria are not significantly clustered, they are distanced from other sources. Pachuca's samples and artifacts, while not clustered significantly, remain separate from Paredon while being relatively close to its samples and artifacts.



Figure 6: Bivariate Plot of Sr by Y

Figure 7 is the biplot comparing Sr to Y. In this plot, Guadalupe Victoria, Otumba, Pachuca, and Zaragoza's samples and artifacts are all clustered significantly and distinctly from each other. Paredon's samples and artifacts are separate from those of the other sources but are not clustered separately.



Figure 7: Bivariate Plot of Zn by Sr

Figure 8 is the biplot comparing Zn to Sr. In this biplot, Pachuca, Otumba, and Guadalupe Victoria are all distanced from other sources, although one Pachuca lies slightly outside of the density ellipse. Though Paredon and Zaragoza are clustered significantly, their density ellipses overlap slightly. Multiple attributions were performed over the course of the statistical analysis process to verify the replicability of the results. Each repetition found the same results; the same sources were attributed to the same artifacts every time. This is despite the overlaps and similarities seen between the Paredon and Zaragoza source samples and artifacts. These repetitions suggest that the sources found are accurate and reliable.

DISCUSSION AND CONCLUSION

This analysis found the five sources of Paredon, Otumba, Guadalupe Victoria, Zaragoza, and Pachuca for the 16 Late Terminal Formative artifacts, utilizing the methodologies outlined above. The observed clustering of the artifacts around the sources is significant, as seen in the significance probabilities of the density ellipses for each source across multiple elemental comparisons. While these artifacts were attributed sources manually in the SAS Jump Pro 12 program, which is a potential source of error, the high number and consistent instances of significant clustering found and the repeated results in multiple assignations suggest that misidentification is unlikely, and errors are negligible. However, in future studies, a sample of the analyzed artifacts in this study could be submitted for Instrumental Neutron Activation Analysis (INAA) or Laboratory XRF to test the accuracy of these results, especially between Paredon and Zaragoza sources.

While five sources were found in the course of this analysis, agreeing with the number found by Williams, the sources were not identical. This analysis did not find Ucareo, while Williams' analysis did not find Paredon (2012, p.98). This could be due to differences in sensitivity between devices or differences in artifacts being analyzed. Not all artifacts analyzed by Williams are present in this analysis, and the lack of clarity within William's analysis makes it impossible to determine which artifacts were identified with each source. This makes it difficult to directly compare differences in identification. However, the identification of five sources does align with William's 2011 analysis, which studied only seven samples from Barber's 2003 excavation of Yugüe (2012, p.95). This indicates that there is some continuity

between analyses of Yugüe obsidian and that the site has been consistently identified with similar numbers of sources.

This analysis has provided valuable information on the sources of individual artifacts. This information has not been previously published, allowing for greater understandings of the artifacts themselves as well as for Yugüe in general. By determining the sources of obsidian artifacts, their life histories can be better understood. Life histories of objects are useful in archaeology because they illustrate how people used objects in the past and illuminate relationships between people, artifacts, and space over time.

The decentralization of the Rio Verde valley at the end of the Terminal Formative period was expected to result in an even distribution of obsidian sources at the site, with relatively equal numbers of obsidian material attributed to each source. In this small sample, Pachuca and Zaragoza are more represented than other three sources, although the distribution of sources is more even than seen in the sample form the Late Postclassic period. This could be a result of sampling error, but this could also be representative of a pattern of shifting source concentrations in the region around the Late Terminal formative, where "the dominant source in the lower Verde shifted from Paredon during the Late Formative to Pachuca by the Early Classic" (Joyce et al., 1995, p.12). Blomster and Glascock (2011, p.38) note that Oaxaca shifted from obsidian sources from the coast of the Gulf of Mexico, such as Guadalupe Victoria and Zaragoza, to sources from central Mexico, such as Paredon, Otumba, and Pachuca, over the Formative period. 9 of the 16 analyzed Later Terminal Formative samples are from these central Mexican sources. Further sampling is needed to elucidate these patterns.

The concentration of Pachuca obsidian in the Late Postclassic is extremely high. This reliance on Pachuca obsidian has also been observed by Levine et al. (2011 pp.129-130) in the Late Postclassic lower Rio Verde valley. They suggest that this is a result of socioeconomic exchange between central Mexico and Oaxaca. This narrowing of sources from the Terminal Formative shows changes in trade patterns that could represent hegemonic political and economic changes that took place through time in the valley. Again, this pattern will need further investigation.

For Yugüe, understanding h130ow and why people used obsidian from different contexts can be used to ascertain aspects of life at the site. If Yugüe has obsidian from only a few sources or from the closest sources when compared to equivalent tertiary sites around Rio Viejo, it could be assumed that Yugüe had limited access to the obsidian trade, or even trade in general. If, however, Yugüe had obsidian from more sources than other sites, it could be assumed that Yugüe had significant access to trade and could be an important regional trade center.

Archaeologists studying Oaxaca and, more specifically, the Rio Viejo Valley would be interested in the trade patterns at Yugüe for a number of reasons. As Yugüe is a tertiary settlement in the valley, by understanding how trade and artifact distribution/sourcing took place in the past, archaeologists can make assumptions about the access to resources and trade patterns of other tertiary sites around Rio Viejo.

Directions for Future Research

The results of this project suggest many future directions for studying obsidian use in the Rio Verde valley.

These data can be used to determine whether different categories of artifacts, such as blades, bifaces, and flakes, had different sources. For example, if eccentric flints are created from obsidian that was formed further away and was traded further than the obsidian used in normal blades, it can be determined that there was a more specific demand for obsidian from further away for more prestigious items or that this type of obsidian was saved for special purposes, rather than used for everyday objects.

The possible connection between Yugüe and the producers of Pachuca obsidian, particularly in the Terminal Formative period, should be examined further. This should then be compared to the concentration of Pachuca obsidian in the Late Postclassic. A larger sample size for both periods could facilitate this comparison.

Through comparison of sources at Yugüe and Rio Viejo, it would be possible to study differential access to resources between sites of different sizes. This would allow for a greater understanding of the lives of both the elite and the common, both of which were necessary for the construction of past societies and are necessary for reconstructing them for present study.

LIST OF REFERENCES

Barber, S. B. (2004, March 8). Proyecto Rio Verde, 2003: Report on excavations at Yugüe.Foundation for the Advancement of Mesoamerican Studies.

http://www.famsi.org/reports/02060/

- Barber, S. B. (2005). *Heterogeneity, identity, and complexity: Negotiating status and authority in Terminal Formative coastal Oaxaca* (Publication No. 3190396) [Doctoral dissertation, University of Colorado]. ProQuest Dissertations and Theses Global.
- Blomster, J. P., & Glascock, M. D. (2011). Obsidian procurement in formative Oaxaca, Mexico:
 Diachronic changes in political economy and interregional interaction. *Journal of Field Archaeology*, 36(1), 21–41. https://doi.org/10.1179/009346910x12707321242278
- Drake, L. [Lee Drake]. (2014, Nov. 5). *XRF Physics* [Video]. Youtube. <u>https://youtu.be/gYaiCcCEjVQ</u>
- Drake, L. (2018). *Filter and voltage*. XRF guru. https://www.xrf.guru/Concepts/FilterAndVoltage/index.html
- Ferguson, J. R. (2012). X-Ray fluorescence of obsidian: Approaches to calibration and the analysis of small samples. In A.N. Shugar & J.L. Mass (Eds.), *Handheld XRF for art and* archaeology (pp. 401-422). Leuven University Press.
- Frahm, E. (2016). Can I get chips with that? Sourcing small obsidian artifacts down to microdebitage scales with portable XRF. *Journal of Archaeological Science: Reports*, 9, 448–467. https://doi.org/10.1016/j.jasrep.2016.08.032

- Glascock, M. D. (2002). Obsidian provenance research in the Americas. *Accounts of Chemical Research*, *35*(8), (pp.611-617). <u>https://doi.org/10.1021/ar010041f</u>
- Joyce, A. A. (2008). Domination, negotiation, and collapse: A history of centralized authority on the Oaxaca coast before the late Postclassic. In Jeffrey P. Blomster (Ed.), *After Monte Alban: Transformation and Negotiation in Oaxaca, Mexico* (pp.219-254). University Press of Colorado.
- Joyce, A., Elam, J., Glascock, M., Neff, H., & Winter, M. (1995). Exchange Implications of Obsidian Source Analysis from the Lower Rio Verde Valley, Oaxaca, Mexico. *Latin American Antiquity*, 6(1), 3-15. doi:10.2307/971597
- Levine, M., Joyce, A., & Glascock, M. (2011). Shifting patterns of obsidian exchange in Postclassic Oaxaca, Mexico. Ancient Mesoamerica, 22(1), 123-133. https://www.jstor.org/stable/26309552
- Liritzis, I., & Zacharias, Z. (2011). Portable XRF of archaeological artifacts: Current research, potentials and limitations. In M.S. Shackley (Ed.), *X-Ray fluorescence spectrometry* (*XRF*) in geoarchaeology (pp.109-142). Springer. 10.1007/978-1-4419-6886-9.
- Migliori, A., Bonanni, P., Carraresi, L., Grassi, N., & Mandò, P. A. (2011). A novel portable XRF spectrometer with range of detection extended to low-Z elements. *X-Ray Spectrometry*, *40*(2), 107–112. https://doi.org/10.1002/xrs.1316
- Shackley, M. S. (2010, November). Is there reliability and validity in portable X-ray fluorescence spectrometry (PXRF)? *The SAA Archaeological Record*, *10*(5), 17-20.

- Shackley, M.S. (Ed.) (2011). X-Ray fluorescence spectrometry (XRF) in geoarchaeology (pp.7-44). Springer. 10.1007/978-1-4419-6886-9.
- Shugar, A. N., & Mass, J. L. (2012). Introduction. In A.N. Shugar & J.L. Mass (Eds.), *Handheld XRF for art and archaeology* (pp. 17-36). Leuven University Press.
- Waite, D. (2020). Household economies and socioeconomic integration: An analysis of obsidian artifacts from Coba, Quintana Roo and Yaxuna, Yucatan, Mexico (Publication No. DP0023191) [Master's thesis, University of Central Florida]. Showcase of Text, Archives, Research and Scholarship. <u>https://purls.library.ucf.edu/go/DP0023191</u>
- Williams, D. T. (2012). Typological and Geochemical Analysis of Obsidian Artifacts: A Diachronic Study from The Lower Rio Verde Valley, Oaxaca, Mexico [Master's Thesis, University of Colorado at Boulder].

https://scholar.colorado.edu/concern/graduate_thesis_or_dissertations/rx913q26p