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GEOCHEMICAL CHARACTERIZATION OF OBSIDIAN SUBSOURCES IN HIGHLAND GUATEMALA

A Thesis in

Anthropology

by

Sean Peter Carr

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The thesis of Sean Peter Carr was reviewed and approved* by the following:

Kenneth Hirth Professor of Anthropology Thesis Advisor Graduate Program Chair

Sarah McClure Assistant Professor of Anthropology

Timothy Ryan Associate Professor of Anthropology and Information Sciences and Technology

*Signatures are on file in the Graduate School

ABSTRACT

This thesis geochemically and geographically identifies obsidian subsources in the Valley of Guatemala and the surrounding region. It particularly focuses on the major source systems of El Chayal, San Martin Jilotepeque, and Ixtepeque. Geochemical traceelement characterizations are made using Portable X-ray Fluorescence (pXRF) spectrometry. The subsources are then mapped onto the landscape using Geographic Information Systems (GIS). The characterization of these subsources increases our understanding of the possible sources from which pre-Hispanic Mesoamericans obtained obsidian. Obsidian subsources are archaeologically significant because the resource had an important role in the ancient economy of the region.

TABLE OF CONTENTS

List of Tables	vi
List of Figures	vii
Acknowledgements	viii
Chapter 1. INTRODUCTION	1
Chapter 2 OBSIDIAN SOURCES SUBSOURCES AND ARCHAEOLOGY	Q
Source Characterization	رو و
Early Source Characterization and Archaeology	10
Mesoamerican Source Characterization Today	10
Subsource Characterization	12
Subsources and Archaeology	13
Subsources and Menacology	15
The Present Research	13
	10
Chapter 3. OBSIDIAN SOURCING TECHNIQUES	20
Sourcing Techniques	20
Visual Sourcing Techniques	21
Neutron Activation Analysis	23
Inductively Coupled Plasma Mass Spectrometry	25
Proton Induced X-ray Emission	
Desktop X-ray Fluorescence	27
Portable XRF Methodology	29
Portable XRF and Archaeology in the Present and Future	32
Chapter 4. THE ZONE-AREA-SECTOR SYSTEM	35
GIS Methodology	38
Chapter 5. GEOCHEMICAL CHARACTERIZATION OF SUBSOURCES	
pXRF Methodology	
Sample Selection	
Instrumentation	46
Operating Procedures	47
Data Analysis	47
The Obsidian Source Systems of Highland Guatemala	49
Intrasource Variation at El Chayal	52
Intrasource Variation at San Martin Jilotepeque	55
Intrasource Variation at Ixtepeque	58

Chapter 6. DISCUSSION	61
The El Chayal Subsources	61
The San Martin Jilotepeque Subsources	62
The Ixtepeque Subsources	63
pXRF and Subsource Characterization in Highland Guatemala	64
Inconsistent Results	64
Conclusion	67
Appendix A. Concentrations for All Samples	69
Appendix B. Source Sampling Localities	75
Appendix C. Mahalanobis Distance Group Membership Probabilities	77
Bibliography	

LIST OF TABLES

Table 5.1 Summary Statistics for El Chayal, San Martin Jilotepeque, and Ixtepeque	.49
Table 5.2 Summary Statistics for El Chayal Subsources	.52
Table 5.3 Summary Statistics for San Martin Jilotepeque Subsources	.55
Table 5.4 Summary Statistics for Ixtepeque Subsources	.58

LIST OF FIGURES

Figure 1.1 The Study Area	2
Figure 1.2 Obsidian Sources of Interest	3
Figure 1.3 The Geographic Distribution of Mesoamerican Obsidian Sources	6
Figure 4.1 The Zone-Area-Sector System	37
Figure 4.2 Kaminaljuyu	39
Figure 4.3 Location of the Kaminaljuyu Acropolis	40
Figure 4.4 Maximum Margin of Error for Geographic Provenience	41
Figure 4.5 The Zone-Area-Sector System Georeferenced to Modern Imagery	42
Figure 4.6 Georeferenced Source Sampling Localities	46
Figure 5.1 Bivariate Plot for El Chayal, San Martin Jilotepeque, and Ixtepeque	50
Figure 5.2 Map of Sampled Source Systems	51
Figure 5.3 Bivariate Plot for El Chayal Subsources	53
Figure 5.4 Map of El Chayal Subsource Assignments	54
Figure 5.5 Bivariate Plot for San Martin Jilotepeque Subsources	56
Figure 5.6 Map of San Martin Jilotepeque Subsource Assignments	57
Figure 5.7 Bivariate Plot for Ixtepeque Subsources	59
Figure 5.8 Map of Ixtepeque Subsource Assignments	60

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Chapter 1: Introduction

This thesis geochemically and geographically distinguishes obsidian subsources in the highlands of Guatemala. While the present research primarily examines the El Chayal source system located northeast of modern-day Guatemala City, the results of samples analyzed from the San Martin Jilotepeque and Ixtepeque source systems are also presented. A combination of geological and geographic techniques is used to accomplish this goal. Portable X-ray Fluorescence (pXRF) spectrometry permits trace-element analysis of obsidian source samples. Statistical techniques such as cluster analysis and bivariate plotting are then used to characterize each of these samples into their respective geochemical subsource groups. Finally, the results are mapped onto the landscape using Geographic Information Systems (GIS) mapping techniques. The significance of the present research will be outlined in this introductory chapter.

While this thesis is based upon previous research in the Valley of Guatemala (Hurtado de Mendoza 1977; Hurtado de Mendoza and Jester 1978), it improves our understanding of obsidian subsources in the region. The present research analyzes obsidian samples collected from a previous source survey (Hurtado de Mendoza 1977:10), but it increases the number of specimens used for geochemical analysis from 179 to 215. Furthermore, all previous analyses were conducted using neutron activation analysis (NAA). This study uses pXRF spectrometry, and consequently permits unique elements of interest to be included for geochemical characterization. While Hurtado de Mendoza and Jester (1978) present data for elemental concentrations unique to NAA, pXRF permits concentrations for a different suite of elements. Fortunately, the trace-element concentrations that can be reliably acquired with X-ray fluorescence have proven to be significant for source characterization in Mesoamerica.



Figure 1.1 The Study Area

Finally, GIS maps will be produced that vastly improve upon the previous geographic provenience from Hurtado de Mendoza's source survey. The implementation of new techniques enhance our understanding of obsidian subsources in the Valley of Guatemala by providing updated geochemical characterizations and accurate geographic provenience.



Figure 1.2 Obsidian Sources of Interest

Archaeologists study obsidian because it was a widely exploited resource in many ancient societies. This is especially true in Mesoamerica, where it played a central role in the economy. As a stone-age society, Mesoamericans relied on obsidian for a wide variety of purposes. Obsidian was present in the everyday lives of most people regardless of differences such as social status or sex. Archaeologically, obsidian artifacts are found in both elite and commoner contexts. Obsidian formed part of the Mesoamerican domestic economy, as it was commonly shaped into tools such as blades and scrapers that were necessary for everyday tasks. It was also used in ritual contexts, since it could be crafted into objects such as masks and beads. Finally, obsidian hafted blades, bifacially worked knives, and projectile points were commonly used in warfare. These are just a few examples that demonstrate obsidian's prominence in ancient Mesoamerica. Therefore, its role in the economy as well as other components of Mesoamerican society cannot be underestimated.

In order to understand the complex economic system by which raw obsidian was procured, distributed, and manipulated to produce finished tools and other goods, one must examine each component of the process by which raw materials from the source ended up as finished, usable blades in households throughout Mesoamerica. Hirth (2012:409-410) stresses the necessity of understanding the entirety of the obsidian *industry system* in Mesoamerica. Obsidian industry systems are not only composed of the tool manufacturing process, but also involve the relationships and networks by which materials were procured, distributed, and consumed. This term fully encompasses the networks of interaction by which obsidian procurement, tool manufacture, and distribution occurred. This thesis in particular will examine sources as a major component of the overall Mesoamerican obsidian industry system. In particular, it contributes to our understanding of how geological and geographical variation within Guatemalan sources influenced the obsidian industry system.

All obsidian occurs naturally at a geological source. Therefore, sources are the logical starting point for understanding human exploitation of obsidian as a natural resource. Archaeologists need to understand the nature of obsidian as it occurs at its geological source. Obsidian is not evenly distributed across the landscape; instead, it only occurs at specific volcanic sources. The deposits at these localities form as a result of volcanic flows that adhere to

specific geological conditions. Therefore, obsidian is a geographically restricted resource, as its procurement requires access to a unique locality. This restriction only increases the value of obsidian, since more energy must be expended to obtain raw materials from specific locations. This must be taken into consideration, since procurement at the source was inevitably a major component of the obsidian economy. Archaeologists who study obsidian should not underestimate the significance of identifying the sources at which it naturally occurs.

In Mesoamerica, obsidian sources are heavily concentrated in two distinct volcanic areas: Central Mexico and Highland Guatemala (Figure 1.3). For this reason, ancient Mesoamerican societies exploited and interacted with the specific localities within these regions where they could procure obsidian for their own use. Obsidian artifacts are distributed throughout the entirety of Mesoamerica's archaeological record; therefore, it is likely that a variety of procurement strategies and economic networks were developed to obtain the necessary raw materials for production. A great number of archaeological questions can be addressed through research at obsidian sources. Which obsidian sources were exploited by different sites at different time periods? What procurement strategies existed at the source? Did different networks of exchange and distribution exist for various sources and sites? Were different sources controlled by elites or other entities? These are just a few examples of the different types of questions that can be explored archaeologically by employing various methodologies. Robert Cobean (2002) stresses the necessity of studying obsidian sources. He characterizes obsidian source areas as "fundamental components of the productive forces which produced Mesoamerican civilization" (Cobean 2002:23). Nevertheless, he points out that archaeologists



Figure 1.3 The geographic distribution of Mesoamerican obsidian sources

for the most part have still not adequately studied obsidian sources. There is still a great deal of work that must be done to understand the economic, social, and political significance of obsidian sources. There is presently an urgent need for more archaeological work to be done at obsidian sources, since they are threatened by looting, deforestation, and other forces of modernization (Cobean 2002:23). The present study hopes to contribute to this by chemically characterizing and mapping obsidian subsources in the Valley of Guatemala to the best extent with all available samples and geographic information in the absence of conducting a comprehensive source survey and mapping project.

Obsidian subsources are useful units of analysis because they are the most specific entity from which raw obsidian was procured in the ancient world that can be identified based on their unique chemical fingerprint. While each obsidian source has a unique chemical composition that is identifiable through various geochemical techniques, there are often significant differences that are observable within sources (Shackley 2005:4). These differences within obsidian source systems are best referred to as *intrasource variation*. Particular outcrops within a larger volcanic source are known as subsources. As a result of different volcanic flows and formation processes, these subsources each have their own unique composition that can be distinguished from other subsources within the overall source area (Hurtado de Mendoza and Jester 1978:424). The identification of the unique chemical signatures of subsources within a larger source area permits geographic origin of a sample of obsidian to be determined with higher precision (Braswell and Glascock 1998; Hurtado de Mendoza 1977). Therefore, an artifact's unique composition can be used to determine the precise area from which its raw material was procured. This is useful knowledge for archaeologists, since source areas often cover a large geographic area. For example in Guatemala, the El Chayal source system covers approximately 525 square kilometers (Hurtado de Mendoza and Jester 1978:433), and the San Martin Jilotepeque source system covers about 280 square kilometers (Braswell and Glascock 1998:356). The probability that these source areas contain multiple subsource groups is high, as such phenomena have been demonstrated in source studies both in Mesoamerica and other parts of the world (Hughes 1988; Hughes 1994; Hurtado de Mendoza and Jester 1978; Braswell and Glascock 1998). The identification of subsources within these systems is particularly essential for microsourcing studies, since it accounts for multiple, precise locations from which obsidian could have possibly been procured (Braswell and Glascock 1998:355). The ability to identify the precise location of procurement sites is undoubtedly of use to archaeologists (Eerkens and Rosenthal 2004).

This thesis will examine research questions that have yet to be addressed. While this introductory chapter has provided an overview of the ways that the present research will make unique contributions to Mesoamerican archaeology, Chapter 2 examines the literature surrounding obsidian sourcing studies and subsource characterizations both throughout Mesoamerica and more particularly in Guatemala. It explores the contributions and shortcomings of previous research and address where improvements will be made. Chapter 3 focuses on different techniques and methodologies used in sourcing studies, as it is imperative to have an understanding of these in order to make accurate interpretations of geochemical data. It argues that pXRF analysis is the most appropriate technique for the present research. Chapter 4 examines the geographic setting of the Valley of Guatemala and its obsidian sources. It discusses the coordinate system that was previously used by Luis Hurtado de Mendoza and explains the GIS techniques that were used to reconfigure it into accurate and accessible geographic data for each of the subsources examined. Chapter 5 presents the data obtained from pXRF analysis. Chapter 6 further examines the results of the geochemical and spatial analysis. It concludes with a discussion of the implications for future research.

Chapter 2: Obsidian Sources, Subsources, and Archaeology

Lithics provide evidence for ancient economic activities such as acquisition, production, distribution, and consumption of goods (Torrence 1986:5). Obsidian sourcing studies use the archaeological record to reconstruct behaviors such as exchange or other possible processes by which an obsidian artifact is found at a different location than its original geological source. Of particular interest are compositional studies, which rely on two variables to make interpretations about behavior: the composition of raw source materials and the spatial distribution of artifacts that can be linked to them (Torrence 1986:4).

Source Characterization

While obsidian provenance studies abound in Mesoamerican archaeological literature (Carballo et al. 2007; Cobean et al. 1971; Dreiss and Brown 1989; Ebert et al. 2014; Golitko et al. 2012; Hammond 1972; Hirth et al. 2013; Moholy-Nagy 2003; Moholy-Nagy et al. 2013), they would not be possible without data from sources themselves. This information is significant for archaeological research, but it is incomplete (Shackley 1998:12; Cobean 2002:35). Present research lacks comprehensive datasets from sources with large samples, consistent methodologies, and accurate geographic information. Future studies need to address these problems. The lack of comprehensive geological and archaeological surveys of Mesoamerican obsidian sources hinders the accuracy of trace-element studies (Cobean 2002:35). Cobean notes that even sources which have already been surveyed "lack sufficient information" (2002:35). This is true for the present research, which is improving upon previous work at sources in the Valley of Guatemala by increasing the sample size, outlining a consistent methodology for a new technique that permits more elements to be used for characterization, and providing more geographic detail.

Early Source Characterization and Archaeology

The first archaeological work on geochemical obsidian sourcing was done by Colin Renfrew, J.R. Cann, and J.E. Dixon in the Aegean (Renfrew et al. 1965). In this vanguard paper, the authors use neutron activation analysis to discriminate 5 unique obsidian sources in the region and then reconstruct trade routes with data from analyses of artifacts at sites. While it may seem at first that archaeologists should only be concerned with the implications of the provenance information gained by the artifact analysis, the authors make sure to note that

"The essential step in establishing the origin of obsidian artefacts is to find grounds for distinguishing the obsidians from the different sources. Only if obsidian from the sources is thus reliably characterized is there any prospect of making valid attributions for the origin of archaeological finds. For this purpose a property or properties are needed which are reasonably consistent for a given source and yet are distinct and characteristic when different sources are compared." (Renfrew et al. 1965:233).

This acknowledges that sourcing studies are not valid without the support of a sample of well characterized source materials. Unfortunately, they only present data from 22 source samples (Renfrew et al. 1965:246-247). According to Cobean, comprehensive source characterizations should ideally be based on analyses of over 100 samples (Cobean 2002:207). Nevertheless, the authors at least acknowledge that source characterizations are an important component of geochemical obsidian studies in archaeology.

With the influence of Renfrew et al. (1965), geochemical obsidian sourcing studies were first introduced into Mesoamerican archaeological research by Robert Cobean, Michael Coe, Edward Parry, Karl Turekian, and Dinkar Kharkar (Cobean et al. 1971). They use X-ray

fluorescence to characterize a large number of Mesoamerican obsidian sources located both in Central Mexico and Guatemala. They determine that trace-element analyses of iron, manganese, rubidium, strontium, and zirconium can be used to geochemically discriminate each of the Mesoamerican sources (Cobean et al. 1971:667). Using these source characterizations, they analyze a sample of obsidian artifacts from the Olmec site of San Lorenzo Tenochtitlan to determine the various sources that were exploited by this major Preclassic site. The elements of interest targeted by Cobean et al. (1971) continue to be significant for Mesoamerican traceelement analyses of obsidian to this day. As the first geochemical obsidian sourcing study in Mesoamerica, this paper has influenced a great deal of obsidian research.

The methodology of Renfrew et al. (1965) for trace-element analysis of archaeological obsidian was further integrated into Mesoamerican research by Norman Hammond (1972). Using X-ray fluorescence, he distinguishes the Guatemalan sources of El Chayal and Ixtepeque (both of which are presently being examined) and maps their distribution at sites throughout the Maya region. He used his results to show that each major Guatemalan source was distributed via unique networks that he concludes were trade routes. While El Chayal obsidian moved north and west into the Maya area through overland routes, Ixtepeque obsidian was transported via the Motagua River to the Gulf of Honduras, at which point it was distributed along the coast of the Yucatan Peninsula. Although Hammond's paper is important for Mesoamerican obsidian studies, it lacks methodological detail and presentation of concrete data. Nevertheless, his conclusions continue to be supported by more recent research (Golitko et al. 2012).

Finally, of particular interest to this thesis are the Guatemalan source characterizations performed by Asaro et al. (1978). In their paper, they present the results of neutron activation analysis of obsidian from El Chayal, Ixtepeque, San Martin Jilotepeque, and Tajumulco. While

their sample sizes are small (n=27 for El Chayal; n=6 for San Martin Jilotepeque; n=2 for Ixtepeque; n=11 for Tajumulco), they provide good data for each source using a reliable technique. They conclude that their results provide a reliable reference for the geochemical compositions of the sampled Guatemalan source, but future research should use another technique such as XRF to obtain concentrations for other elements of interest such as Ti, Ca, Sr, and Zr (Asaro et al. 1978:442).

Mesoamerican Source Characterization Today

With the influence of the early research of Renfrew et al. (1965), Cobean et al. (1971), Hammond (1972), and Asaro et al. (1978), geochemical obsidian studies continue to be prevalent in Mesoamerican archaeology. While the earliest papers used their own source characterization data from a small sample that they collected as part of their interest in obsidian provenance at sites, efforts have since been made to establish a uniform database of source characterizations drawn from a wide range of samples that encompass all possible variation. The earliest example of this was published by Cobean et al. (1991). In this paper, the authors use neutron activation to analyze 208 geological samples from 25 different Mesoamerican source areas. Neutron activation proves to be an effective technique not only for the accuracy and precision of its results, but also for its ability to obtain readings for 28 elements of each sample.

Robert Cobean further synthesized Mesoamerican obsidian source data in *A World of Obsidian* (2002). This has proven to be the most comprehensive compilation of source data, although it only encompasses Mexican obsidian sources. Unfortunately, there is no such manual for Guatemalan obsidian sources. Future research should aim to synthesize data from Guatemalan sources as Cobean has done in Mexico. The research reactor at the University of

Missouri currently hosts the largest database of Mesoamerican geochemical obsidian data. Large datasets such as this that are freely available to other researchers are important for sourcing studies, as results will only continue to be strengthened with more robust samples analyzed with a consistent methodology.

Subsource Characterization

This thesis is not concerned with obsidian characterization at the larger source level, but rather intends to make determinations at a smaller, more precise geographical and compositional scale. Although all obsidian within a source area is geochemically distinguishable, precise subsources with distinct chemical fingerprints can be reliably identified within source areas as the result of numerous volcanic events (Cobean 2002:31). This phenomenon is defined by Braswell and Glascock (1998) as *intrasource variation*. While such variation was not initially addressed in the archaeological literature, it has increasingly become an important subject for those interested in archaeological obsidian studies.

Subsources and Archaeology

Luis Hurtado de Mendoza's (1977) doctoral dissertation is one of the earliest pieces of research that recognizes geochemical variation within source areas. While he was primarily interested in the variation of hydration rates within Guatemalan obsidian sources, he conducted a comprehensive source survey and was able to geochemically distinguish a number of subsources within the Valley of Guatemala. He later published his results in a paper on the geochemical variation he observed within the subsources he sampled (Hurtado de Mendoza and Jester 1978). Unfortunately, there are a number of problems with this research including an inadequate sample size. While the authors present data for 179 analyses, this thesis increases the sample to 215

source specimens for pXRF spectrometry. Furthermore, their analysis omits important trace elements including strontium and zirconium that could have been incorporated into the analysis.

Richard E. Hughes (1988) focused on the archaeological implications of intrasource variation at the Coso source in California. He distinguishes four unique subsources within the Coso source area using a combination of XRF analysis and bivariate statistical routines plotting concentrations of zirconium and rubidium (Hughes 1988:259). He concludes that such variability is significant for archaeologists in all parts of the world where obsidian is present, since he believes that the variability observed at Coso is likely to occur elsewhere. Subsource variation can be used to understand changes in utilization at the source over time. Furthermore, he asserts that variability cannot solely be predicted based on geographic location, since flows often overlap or mix with other materials. Geochemical variability exists within source areas, and it is necessary to demonstrate this with appropriate techniques. Hughes (1994) later conducted similar research at the Casa Diablo source area in California. Once again, he is able to make subsource determinations based upon variation in geochemical concentrations. He concludes that this type of variation is significant not only for archaeologists who are interested in obsidian hydration rates, but furthermore, for those who are interested in provenance studies with the highest possible degree of accuracy. Hughes' research provides some of the earliest and best discussions of the archaeological significance of intrasource variation.

The question if obsidian subsources in archaeology are meaningful units of analysis specifically examined in a paper by Eerkens and Rosenthal (2004). They identify the spatial and temporal distribution of obsidian from Coso, California's subsources. Their results indicate that obsidian subsources are not only significant for obsidian hydration rates, but can also provide insight into different patterns of obsidian exploitation at a smaller scale. Their analysis of

artifacts from sites in the region provides evidence for spatial and temporal variation of obsidian subsources (Eerkens and Rosenthal 2004:24). The authors further assert that similar patterns could be observed within other source areas to obtain a better understanding of prehistoric quarrying, exchange, resource exploitation, and landscape use (Eerkens and Rosenthal 2004:28). Therefore, obsidian subsourcing techniques have great potential for archaeological research in parts of the world where obsidian was exploited in prehistoric society. Despite the ubiquity of obsidian in ancient Mesoamerica, subsourcing studies are scarce. There is great potential for future subsource characterization studies in Mesoamerican archaeology. The following sections will examine the state of obsidian subsourcing research in Mesoamerica as it stands today.

Subsourcing in Mesoamerica: Previous Research

Only 4 of the 37 Mesoamerican obsidian sources identified by Cobean (2002:27) have been characterized at the subsource level. These include Pachuca (Argote-Espino et al. 2012; Cobean 2002), Otumba (Argote-Espino et al. 2012), San Martin Jilotepeque (Braswell and Glascock 1998), and El Chayal (Hurtado de Mendoza and Jester 1978).Furthermore, each of these subsource characterizations could be improved with increased sampling and/or geographic provenience data. An examination of each of these provides necessary information when designing a subsource characterization study for a Mesoamerican obsidian source.

Hurtado de Mendoza and Jester (1978) provide the first subsource characterization study in Mesoamerica. Consequently, the present research builds upon their work by analyzing materials from the Valley of Guatemala survey conducted by Hurtado de Mendoza and relying on his project's coordinate system for the location of subsources within region. While Hurtado de Mendoza and Jester's paper is one of the first of its kind, it is problematic for a number of reasons. For their neutron activation analysis, they analyze a total sample of 179 geological specimens and are able to determine 11 distinct "source subsystems" in their Guatemalan samples (Hurtado de Mendoza and Jester 1978:432). A major problem with the previous subsourcing work done for the El Chayal source and the surrounding area is its geographic provenience. Their source survey recorded all geographic information only with respect to the Penn State Project's Zone-Area-Sector system. While this system will be discussed in much further detail in Chapter 4 of this thesis, its main problem is that the geographic coordinates are based on an antiquated system that requires a great deal of transformations and georeferencing on a GIS map to obtain the actual geographic coordinates for the subsources. This thesis attempts to improve upon the work of Hurtado de Mendoza and Jester (1978) by addressing its shortcomings as well as those of other subsourcing studies that have been done in Mesoamerica.

Perhaps the most methodologically sound Mesoamerican subsourcing research was done by Braswell and Glascock (1998) at the Guatemalan source of San Martin Jilotepeque. Their paper analyzes 69 source specimens within an area of 280 square kilometers using neutron activation analysis. As a result, they are able to discriminate 6 unique subsources. While their sample size is substantial, Braswell and Glascock also employ more comprehensive statistical techniques than Hurtado de Mendoza and Jester (1978) in the previous Guatemalan subsourcing study. Another great advantage of this study is that each sampled locality was carefully mapped and therefore the subsource areas are associated with a clear geographic location in the publication. For these reasons, Braswell and Glascock (1998) provide a great demonstration of an effective methodology that can be used as a model to determine obsidian subsources throughout Mesoamerica.

Two subsource characterizations have been done for the Pachuca obsidian source. The first of these is presented in Cobean (2002). Although he does not make any explicit comments about intrasource variability at Pachuca, the geochemical data is presented in three separate groups: Sierra de Pachuca-1, Sierra de Pachuca-2, and Sierra de Pachuca-3 (Cobean 2002:268-270). While Cobean's groups show variation, his characterizations are problematic for a number of reasons. He has a more than adequate sample size for Sierra de Pachuca-1 (n=129), but his sample sizes for Sierra de Pachuca-2 (n=11) and Sierra de Pachuca-3 (n=27) should ideally be increased. He notes that a minimum of 12 samples need to be analyzed for any given geochemical group, but an ideal sample size would permit for over 100 separate analyses (Cobean 2002:207). While his sampling of Sierra de Pachuca-1 meets these criteria, Sierra de Pachuca-2 is below his minimum sample size, and Sierra de Pachuca-3 is on the lower end of the sampling spectrum. Furthermore, Cobean was unable to identify accurate concentrations for strontium, which is an important trace element for Mesoamerican obsidian characterization. The scale of his project is not concerned subsource variation at a single source. As a result, Cobean does not provide adequate subsource information for Pachuca. He notes the need for further research when he says, "Even though the Sierra de Pachuca is the most intensively studied obsidian source in Central Mexico, the limits and internal structure of its flow systems...are unknown" (Cobean 2002:47).

Argote-Espino et al.'s (2012) work is specifically aimed to identify subsources at both Pachuca and Otumba. The main problem with their research is that their sampling strategy is deficient because it is financially constrained (Argote-Espino et al. 2012:54). They use LA-ICP-MS to obtain concentrations for each sample, and although this should provide reliable results, it would be ideal to have a much larger sample to account for all possible variation. They note that

financial constraints only permitted them to analyze 16 samples from Pachuca and 19 samples from Otumba (Argote-Espino 2012:54). Unfortunately, high costs associated with geochemical analyses are another factor that constrain sourcing studies.

In conclusion, previous subsourcing studies in Mesoamerica have generally encountered a variety of problems. Hurtado de Mendoza and Jester (1978) rely on a very small sample and provide problematic geographic provenience for the El Chayal subsources. While LA-ICP-MS is a reliable analytical technique, Argote-Espino et al. (2012) are constrained by financial resources and are only able to analyze a small number of geological samples from both Otumba and Pachuca. Cobean's (2002) overview of Central Mexican sources characterizes three separate groups within the Sierra de Pachuca source system, but at least one group (Sierra de Pachuca-2) does not have a large sample, and he notes that his characterizations are probably not comprehensive enough to cover the entire range of the source (Cobean 2002:47). Finally, Braswell and Glascock (1998) provide the best example of an effective Mesoamerican geochemical subsourcing study. The present research hopes to build upon their methodology and even expand it by analyzing a larger number of geological specimens from a wider range of sampling localities.

The Present Research

The present research improves upon past studies in several ways. It is the first subsourcing research conducted using Portable X-ray Fluorescence in Mesoamerica. Second, it builds on previous work of Hurtado de Mendoza and Jester (1978) by increasing the sample size. Third, it expands the precision of geographic provenience by referencing the Zone-Area-Sector system to UTM coordinates. The implementation of pXRF as a new technique permits the

analyst to obtain accurate concentrations of many elements of interest. This thesis builds upon previous studies to provide a unique contribution to archaeological research that should not only improve our understanding of the subsources within the Valley of Guatemala, but also influence future research of intrasource variation in Mesoamerica.

Chapter 3: Obsidian Sourcing Techniques

This chapter examines different analytical techniques used by archaeologists for obsidian source characterization. It reviews the most common methodologies used by archaeologists for obsidian sourcing and briefly discusses case studies of each. While sourcing studies have been prevalent in archaeology for some time, techniques have different benefits and drawbacks. This chapter examines the pros and cons of various methods that are commonly used. It then explains the reasons why portable X-ray fluorescence (pXRF) is the most appropriate technique for the present research.

Sourcing Techniques

There are a number of methods that can be used to assign a sample of obsidian to a specific source. These range from simple visual sourcing techniques that rely on physical characteristics, to advanced geochemical techniques that use specialized equipment and require statistical manipulations of data using computer software to be interpreted. Archaeologists now have access to various tools that can be used to their advantage. Researchers often desire a simple answer to which of these techniques is the best method for performing analyses. However, there is no straightforward answer, since the most appropriate technique varies between research projects based on a number of circumstances (Shackley 1998:7). Constraints with regard to time, cost, availability, accuracy, and the elements to be measured are just a few examples of the variables that must be considered when determining which technique is appropriate (Glascock et al. 1998:19). Researchers should familiarize themselves with each analytical technique in order to determine which will best meet their needs. It is important to understand how each of these tools work, so that the appropriate measures can be taken when using them and interpreting the results they produce. Furthermore, archaeologists should be

concerned with the practicality of each of these tools. A full understanding of the benefits and drawbacks of each tool permits a consideration of all options when designing research. Therefore, the theory, methodology, and practicality of the most popular sourcing techniques merit examination.

Visual Sourcing Techniques

Some archaeological research has made source designations for samples of obsidian based on observed visual characteristics. Physical traits such as the color in transmitted or reflected light, refractive index, fracture characteristics, opacity, internal structure, and luster can be used to identify differences in obsidian (Glascock 1998:18). While techniques that primarily rely on these characteristics are inexpensive and fast, there are many potential problems with their results (Ferguson 2012:403). Visual sourcing techniques are subjective, and they leave much opportunity for human error to influence their results. They rely on the identification of qualitative traits, rather than using quantitative data. While obsidian sources usually appear to have consistent visual characteristics, there is always some variation within sources. Furthermore, visual techniques make it more difficult to identify subsources, since they are not able to identify the unique chemical fingerprints associated with different volcanic flows. Many sources have unique appearances that should leave little room for doubt when assessing samples visually, but this can still be problematic. For example, the Central Mexican source of Pachuca is notable for its characteristic green color. Nonetheless, archaeologists at sites in the American Southwest have wrongly identified Pachuca obsidian since there are other sources of green obsidian that exist in the region (Ferguson 2012:403). Furthermore, archaeologists usually do not work with obsidian that has a distinct color such as Pachuca. It is possible to work in areas where obsidian samples from different sources have very similar visual characteristics. For these

reasons, visual sourcing techniques are problematic, and archaeologists should not be comfortable accepting their results (Ferguson 2012:403). This said, a number of studies have been done with this methodology that claim to be successful.

Aoyama et al. (1999) published their research on obsidian sources in Honduras that incorporated visual sourcing techniques to identify the source of artifacts from the site of San Luis. To reduce skepticism, the authors compared the results of their visual source analysis to 100 samples analyzed by neutron activation. To this end, they correctly identified the source of 98 percent of all samples (Aoyama 1999:241). Furthermore, they provided a detailed list of the criteria that were used to identify sources. Nonetheless, this success rate may not hold true for other analyses with larger samples. The results of provenance studies that rely on visual source analysis should be viewed with a great amount of uncertainty. Glascock et al. (1998:18) note that visual analyses are only of use when they are supported by more advanced techniques. This is affirmed by Braswell et al. (2000) who successfully conducted a visual analysis supplemented with data from a limited sample analyzed by neutron activation. They argue that when it is combined with a small sample of geochemical data, visual analysis performed by highly experienced researchers provides a reliable and efficient method of analysis (Braswell et al. 2000:278). This conclusion is based upon the obstacles of time, cost, and destructiveness associated with geochemical techniques. They posit that "it is unlikely that NAA, XRF, or other methods of compositional assay will ever be used routinely to source large samples or entire collections of Mesoamerican obsidian artifacts" (Braswell et al. 2000:270). Fortunately for archaeologists interested in obsidian sourcing studies, this statement has become outdated with the rise of new analytical technologies such as pXRF that permit rapid, efficient, and accurate compositional analyses of large samples. Moholy-Nagy (2003:302) appropriately likens the

conclusion of Braswell et al. (2000) to "recommending that people ignore their clocks and watches and learn to tell time by the sun."

Neutron Activation Analysis

While visual sourcing techniques should be viewed with skepticism, geochemical sourcing permits quantitative compositional analysis of obsidian with a high degree of accuracy and precision. Among the geochemical techniques used by archaeologists, neutron activation analysis (NAA) is often considered the most accurate (Shackley 2005:89). This technique was one of the first geochemical sourcing methods to be adopted by archaeologists. While it has been used to obtain the chemical concentrations of many different archaeological materials, NAA is of particular use for obsidian sourcing studies (Hurtado de Mendoza 1977:28). To obtain chemical concentrations using NAA, samples are crushed and encapsulated for irradiation at a nuclear reactor (Glascock and Neff 2003:1522). During irradiation, atoms gain additional neutrons and emit characteristic wavelengths as a result (Hurtado de Mendoza 1977:42). After a period of irradiation, peak concentrations of a wide range of elements can be determined using a detector (Hurtado de Mendoza 1977:38). The use of automatic and computerized instruments to detect the elemental compositions of irradiated samples is commonly referred to as instrumental neutron activation analysis, or INAA (Glascock 2014). Glascock et al. (1998:20) state that neutron activation can be used to determine concentrations of the following elements: 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, Zr. The University of Missouri's Archaeometry Laboratory states that they can identify concentrations of between 25 and 30 elements for obsidian using neutron activation (Glascock 2014). However, the results of NAA are more reliable for some elements than others, especially lighter ones.

There are many examples of neutron activation analysis studies of obsidian in the archaeological literature. Asaro et al. (1978) conducted neutron activation analysis to characterize some of the major Guatemalan obsidian sources. Hurtado de Mendoza (1977) successfully used neutron activation to characterize subsources in the Valley of Guatemala, and Braswell and Glascock (1998) did a similar study at the source of San Martin Jilotepeque. Cobean et al. (1971;1991) implement neutron activation to characterize obsidian from San Lorenzo Tenochtitlan, and Hirth et al. (2013) build upon this work. These are just a few examples of successful studies that rely on NAA to make archaeological interpretations.

While NAA is a reliable chemical sourcing technique, it has several drawbacks that archaeologists must account for when designing their research using this method. The positives of neutron activation include the fact that it permits the identification of a larger range of elements than any other technique (Shackley 2005:89). Furthermore, it usually provides the most reliable results, since its results present the least variation between different labs. Nevertheless, there are a number of factors that can make this technique not appropriate for some research. Neutron activation is a destructive form of analysis, since it requires samples to be cut and pulverized in preparation for irradiation. Therefore, it does not completely preserve the artifacts that are analyzed. This can be problematic for specimens that must be returned to a museum or returned to their country of origin (Shackley 2005:90). NAA is also the most expensive sourcing technique when both temporal and financial costs are considered. Furthermore, not every archaeologist has access to the facilities necessary for this technique, and time must be added for the transportation of samples. When samples are sent away to a lab such as the University of Missouri Research Reactor Facility (MURR), the price per sample analyzed is costlier than any other method (Glascock 2014). Although neutron activation enables archaeologists to determine

the chemical composition of a sample of obsidian with a very high level of accuracy and a wider range of elements to be measured, it is not always the most practical method. Its constraints are problematic, as they may restrict the number of samples that can be analyzed. In the field of archaeology today, funding is often a problem, and there is pressure to obtain, gather results, and publish them at a faster pace than ever. Therefore, neutron activation is only an ideal sourcing technique when funding is available, time is not pressing, and samples can be destroyed.

Inductively Coupled Plasma Mass Spectrometry

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is another sourcing technique that archaeologists commonly use for a variety of materials. When a laser is used to vaporize a small portion of the sample for analysis so that the technique is minimally destructive, it is known as laser ablation inductively coupled mass spectrometry (LA-ICP-MS). This technique is especially effective with samples of obsidian because it permits for elemental concentrations for a wide range of elements to be obtained (Carballo et al. 2007:31). This was demonstrated by Carballo et al. (2007), who successfully sourced obsidian from Formative and Classic period sites in Central Mexico using LA-ICP-MS. Furthermore, Argote-Espino et al. (2012) used this technique to make subsource identifications at the Central Mexican obsidian complexes of Otumba and Pachuca.

As with all sourcing techniques, LA-ICP-MS has benefits and drawbacks. LA-ICP-MS is a favored technique since it is considered to be non-destructive. In reality, this method still destroys a very small part of the sample (Ferguson 2012:404). Therefore, it is not completely non-destructive, but rather less destructive than neutron activation. LA-ICP-MS is also often favored over techniques such as X-ray Fluorescence (XRF) because it accounts for a wider range of elements, similar to NAA (Carballo et al. 2007:30; Ferguson 2012:404). Yet, the resulting

data cannot be considered as accurate as that of neutron activation analysis, and there are often problems with calibration techniques (Ferguson 2012:404). Nevertheless, this method is still considered to be efficient for both time and cost, since analysis is both shorter and less expensive than neutron activation (Carballo 2007:30).

Proton Induced X-ray Emission

Proton Induced X-ray Emission (PIXE) is another geochemical sourcing technique that archaeologists have used to their advantage. This technique is similar to XRF, since it is another method by which x-ray and gamma ray emissions from a specimen are converted into elemental concentrations using a calibration (Ferguson 2012:404; Seelenfreund et al. 1996:14). Samples are placed in the line of a proton beam, and characteristic wavelengths are returned and converted for a range of elements (Seelenfreund et al. 1996:14-15). Seelenfreund et al. (1996) performed a compositional analysis of obsidian from Chile and Argentina that utilized PIXE techniques. With this methodology, they were able to successfully identify a number of different sources that were exploited by sites in their study region (Seelenfreund et al. 1996:9). They acknowledge that their results were adequately precise and accurate when compared to other methods, although they repeatedly had problems with readings of iron and zirconium (Seelenfreund et al. 1996:15). This could be problematic, especially since both of these are elements of interest for Mesoamerican obsidian source compositional studies. It is possible that there were problems with the calibration they used to convert their results into concentrations of parts per million (ppm). Obstacles such as this must be kept in mind when using PIXE to make archaeological interpretations.

Desktop X-Ray Fluorescence

XRF sourcing techniques have been widely used by archaeologists for decades. Using xray spectrometers, the chemical composition of a sample can be determined with high levels of precision and accuracy. Since the early years of x-ray fluorescence, three types of XRF spectrometers have become available to perform compositional studies: wavelength dispersive spectrometers, electron microprobes, and energy dispersive spectrometers (Shackley 2011:10). Wavelength dispersive spectrometers use a crystal to separate the wavelengths of the fluorescence from samples (Shackley 2011:10). Electron microprobes use an electron beam to excite x-rays from the samples that they analyze (Shackley 2011:10). Today, energy dispersive XRF spectrometers (ED-XRF) are the most popular instruments, since they are able to read a wider range of wavelengths than other types of instruments (Ferguson 2012:404). There are a number of examples in the archaeological literature that have successfully performed obsidian provenance studies using these techniques.

It is important to understand the theory behind x-ray fluorescence when performing archaeological studies and assessing their validity. XRF functions by bombarding a sample with x-rays, which have short wavelengths and high frequencies (Shackley 2011:16). When this highenergy radiation interacts with the atoms of the sample that it bombards, they ionize, releasing electrons from their shells (Shackley 2011:16). If electrons from the inner-shell are released, they are replaced by electrons from the outer shell. When this phenomenon occurs, energy with characteristic wavelengths is released. This "fluorescence" is then measured and used to interpret the chemical composition of the sample (Shackley 2005:96). The characteristic wavelengths that are released are converted into parts per million (ppm) of the element that they represent using a calibration that has been developed from standards with known compositional properties.

As with the other aforementioned souring techniques, XRF has both positive and negative aspects. XRF is not able to analyze as wide a range of elements as other techniques (Shackley 2011:10). Furthermore, samples must meet certain size requirements to obtain accurate readings (Shackley 2011:9). Nevertheless, XRF provides archaeologists with a number of benefits that can be used to their advantage. Although neutron activation measures a wider suite of elements, it fails to accurately measure some important trace elements. These include strontium, zirconium, rubidium, and titanium. The measurement of these elements is advantageous for XRF, since significant differences in the concentrations for both of these are observable among Mesoamerican obsidian sources. Unlike NAA and LA-ICP-MS, XRF is a non-destructive analytical technique (Shackley 2011:8). XRF is also time-efficient, since samples do not require any preparation, and accurate readings can be obtained in a few short minutes (Shackley 2011:8-9). Finally, XRF analysis is less expensive than other techniques (Glascock 2014). XRF is a popular and useful technique for archaeologists performing provenance studies.

Having discussed the options that archaeologists have to perform obsidian sourcing techniques, it is clear that all options must be considered and weighed against each other when designing a provenance study. Of all of these techniques, XRF is the most efficient and accessible for archaeologists interested in analyzing large sample sizes. This is especially true of more recent years, due to the rise of portable XRF (pXRF) technology as a tool that is becoming increasingly available for researchers across many disciplines (Shackley 2011:12). This method of analysis is based on the same principles as lab XRF techniques, but it provides archaeologists with new levels of flexibility and accessibility that have never been available for sourcing studies. Portable x-ray fluorescence is increasingly becoming an important component of
archaeological research, and it provides a promising new method of analysis for obsidian sourcing studies.

Portable XRF Methodology

Much of the theoretical and methodological aspects of portable x-ray fluorescence (pXRF) are identical to those of desktop XRF. Differences between the two techniques can be attributed to the portability of the instrument, and archaeologists must account for this while performing analyses and interpreting their results. Since this new technology was developed and became easily accessible, researchers across many disciplines have used pXRF to their advantage (Speakman 2012:1). In archaeology, it has been used in a number of different contexts. In particular, pXRF has been used to obtain the chemical composition for various aspects of the material culture of the past, including ceramics and stone tools. Furthermore, some archaeologists have used pXRF to analyze sediments, soils, pigments, and other materials encountered in the field. The portability, accessibility, and accuracy of pXRF analysis make it an important technique that can make many contributions to our understanding of the past. Nevertheless, it is critical that archaeologists understand the methodology and take appropriate measures to ensure accurate results.

Craig et al. (2007) conducted a useful study that tested the effectiveness of pXRF analysis in archaeology. In this paper, they analyzed Peruvian obsidian samples using both desktop and portable XRF techniques. They note that while the theory behind both techniques is similar, some measures must be taken when using pXRF to ensure consistent results (Craig et al. 2007:2015-2016). In particular, although the instrument is portable, they make sure to keep the instrument stably mounted throughout analyses (Craig et al 2007:2016). This is a necessary measure that should be taken by all archaeologists who perform sourcing analyses of obsidian

with pXRF, since the irregularity of samples and nature of the x-rays produced by the instrument require consistency for both geometry and distance (Craig et al 2007:2016). This approach discourages the "point-and-shoot" approach to pXRF analysis that some archaeologists envision when they are not familiar with the necessary methodological measures (Ferguson 2012:405). Nevertheless, Craig et al. (2007) find the results of the pXRF analysis to be consistent with those of desktop XRF. They conclude that archaeologists can use pXRF to analyze obsidian and obtain results that are just as reliable as other geochemical sourcing techniques.

It is necessary that analysts use the proper calibration. The standards of a calibration must encompass a wide range of elemental concentrations so that all possible concentrations in unknown samples can be detected (Ferguson 2012:406). A good calibration ensures that accurate concentrations with reproducible results will be acquired from each sample (Speakman 2012:2). Problems with calibrations have proven to be one of the main issues surrounding pXRF analysis, and this has been widely debated in the literature (Frahm 2013a, 2013b; Speakman and Shackley 2013). Many have addressed this issue, and efforts have been made to test calibrations that come with pXRF instruments, such as that by Bruker (Speakman 2012). Speakman (2012) analyzes a number of samples with known elemental concentrations for a long period of time, and obtains accurate results with low variability. Nonetheless, issues with calibration continue to be problematic for the accuracy and reproducibility of archaeological provenance studies.

The physical dimensions of a sample can also affect pXRF analyses. Samples should be analyzed at a point where the surface is as flat as possible along the surface of the instrument's sensor. This is necessary to ensure geometric consistency when x-rays make contact with the sample. Samples need to be adequately thick so that x-ray scatter does not influence results (Ferguson 2012:413). When a sample is not thick enough, it will be reflected in the total "valid"

count of fluorescent rays that are read by the detector, and skewed results should be expected. It is also necessary for a sample to be large enough so that it covers the entire sensor of the instrument for this same reason. Analysts must ensure that all of these measures are accounted for when they select samples and perform analyses so that accurate results will be obtained.

pXRF instrumentation also influences results. When conducting analyses, archaeologists must make choices about the instrument that they use so that they can obtain the most accurate results. pXRF spectrometers are currently produced by a number of manufacturers, and they are becoming increasingly available to researchers at a reasonable cost. The instrumentation used for these techniques is an essential component of research design, since different results can be produced under different conditions. The x-ray tube itself will influence results, since tubes of different compositions can be more appropriate for identifying various elemental concentrations (Shackley 2011:26). While most instruments use a tube with a rhodium target for obsidian analysis, a silver tube is appropriate for other materials since it can detect lighter elements (Shackley 2011:27). A filter is often used to maintain energy at an optimum level (Shackley 2011:28), and filters are available that are specifically designed for obsidian analysis. The detector is also an important component of the instrument, since it is responsible for reading characteristic wavelengths that are then converted into parts per millions.

When performing analyses, archaeologists must also ensure that the proper settings are being used to optimize results. Voltage and current influence the results, and Shackley (2011:28) suggests that they should be optimized based on the absorption energy of the elements of interest. Analysts should run samples at a consistent duration of time. While it cannot hurt to analyze a sample for as long as possible, consistent results are almost always obtained within three minutes (Craig et al. 2007:2016; Shackley 2011:31). Analysts must adjust all of these

settings so that the best results can be obtained for the elements of interest from their samples. Furthermore, it is important to report these settings along with their data so that the results are reproducible.

It is clear that archaeologists must account for a number of different influences that can be problematic when performing pXRF sourcing analysis. It is essential that the theoretical and methodological aspects of x-ray fluorescence are properly understood. Furthermore, correct choices must be made with regards to instrumentation so that accurate and precise results can be obtained for elements of interest. As long as these variables are accounted for, pXRF is a powerful tool that can be used to the advantage of archaeological research. It is extremely efficient with respect to both cost and time of analysis, and it is becoming increasingly accessible to archaeologists. Furthermore, pXRF is a non-destructive technique, which is often a concern for the analysis of archaeological materials. Finally, it is portable, which permits flexibility for the location of analysis. Taking these benefits into account, it is apparent that pXRF holds an important place in the future of archaeology.

Portable XRF and Archaeology in the Present and Future

Recently, archaeologists have increasingly recognized the potential for pXRF in their research. This technique has been used to obtain the chemical composition of a number of different archaeological materials, including ceramics, metals, and sediments. The analysis of these materials each has their own caveats and variables that must be accounted for to obtain accurate results. It is important to understand the characteristics of the matrix of any sample that is being analyzed, and in the case of heterogeneous materials, results can be skewed. In addition to understanding the properties of the material being analyzed, archaeologists must also understand the proper techniques and scientific methodology to conduct research that is accurate

and reproducible. All of these issues are at the center of debates surrounding the appropriate uses of pXRF in archaeology today. Similar to the rise of other technologies in archaeological research, it is debated whether pXRF is a tool or a science (Frahm 2013a, 2013b; Speakman and Shackley 2013). Other debates criticize the practice of "silo science", by which results are published but are not reproducible (Speakman and Shackley 2013). Archaeologists interested in the use of pXRF for their own research must be aware of these debates and make informed decisions about these matters. Portable XRF holds a promising future in archaeological research as long as researchers are cognizant of these issues.

While pXRF analysis can be performed on a number of different archaeological materials, many recognize that obsidian is one of the best materials to obtain accurate results. This is due both to the homogenous chemical nature of the glass, as well as the ability of pXRF to accurately measure the target elements of rubidium, strontium, and zirconium (Ferguson 2012). Therefore a number of obsidian provenance studies have been recently published that rely on pXRF. Craig et al. (2007) analyzed obsidian from Peru and demonstrated that the results from pXRF are comparable to those of XRF. Golitko et al. (2010) use pXRF to analyze obsidian in Papua New Guinea to understand movement and interaction between different sites. Ebert et al. (2014) use pXRF to analyze a large sample of artifacts from La Zanja, a Mesoamerican site on the Pacific coast. These are just a small number of studies that serve as examples of the ways that archaeologists can use pXRF to efficiently and accurately perform research.

Although the literature is increasingly filled with archaeological applications of pXRF analysis, some problems remain. An example of this is seen in the recent debate in the Journal of Archaeological Science that pits Ellery Frahm against Robert Speakman and M. Steven Shackley. This began when Frahm (2013a) published a study in which he claims that it is not

necessary to use an accurate calibration, since results will always be internally consistent. This infuriated Speakman and Shackley, who immediately responded (2013). They condemned Frahm's endorsement of "silo science", a practice by which irreproducible results are published. This is problematic, since it requires the reader to simply accept the author's results as valid. Archaeologists need to take the proper scientific steps when publishing geochemical results obtained from pXRF analysis.

This chapter has demonstrated that pXRF is a powerful tool for archaeologists performing obsidian provenance studies. The geologic properties of obsidian permit archaeologists to determine the spatial origin of artifacts through geochemical characterization. While there are a number of available techniques to perform these studies, each has its benefits and problems. Portable XRF is advantageous for archaeological studies of obsidian since it can efficiently analyze large samples with high degrees of flexibility and accuracy. If archaeologists understand the theoretical and methodological aspects of pXRF, then they can use this technique to publish accurate and reproducible results.

This thesis uses pXRF to make geochemical subsource characterizations. The efficiency of pXRF analysis with respect to time and cost of analysis permits a larger number of samples to be analyzed than with any other technique. Furthermore it is a non-destructive technique, which will permit other analyses of the obsidian source samples to be conducted in the future if necessary. X-ray fluorescence also provides accurate geochemical information for certain elements of interest for Mesoamerican obsidian such as strontium, rubidium, and zirconium that are not reliably identified using other techniques. For these reasons, it is the most appropriate analytical technique to determine subsource characterizations for the present research.

Chapter 4: The Zone-Area-Sector System

In addition to identifying geochemical variation within sources, a major goal of this thesis is to provide geographic data for each of the subsources identified in the Valley of Guatemala. This is especially necessary for the El Chayal source area that this research is mainly focused on, since it has not yet been done completely. As with any source or subsource system, geochemical data can only be used to its full potential if compositional signatures can be associated with their place in geographic space. Braswell and Glascock (1998) address this in their study of subsource identification for the San Martin Jilotepeque system. They make it clear that the term "subsource" has both geochemical and spatial implications; therefore, in order to truly identify obsidian subsources, geographic data must be incorporated (Braswell and Glascock 1998:365). This proves to be a challenge for the present research, since Hurtado de Mendoza's source survey during which the samples analyzed were collected does not provide precise geographic information. This thesis addresses this problem through the use of Geographic Information Systems (GIS) techniques.

All of the obsidian sources sampled for this thesis are distributed throughout the highlands of Guatemala. The majority of the localities that were sampled are part of the El Chayal source, which is less than 20 kilometers northeast of modern-day Guatemala City and about 25 kilometers northeast of the major archaeological site of Kaminaljuyu. The second source is San Martin Jilotepeque, named after a nearby town. It is located about 50 kilometers northwest of Guatemala City. Finally, a number of analyzed samples are from the Ixtepeque obsidian source, located in Southeastern Guatemala near the borders of Honduras and El Salvador. All of the sampled areas have been mapped for the present research project. The samples from the El Chayal and San Martin Jilotepeque source regions fall within the

Kaminaljuyu Project's coordinate system (discussed below) and could be mapped once this system was georeferenced to satellite imagery. The only available geographic data for the Ixtepeque sampling localities was an association with modern town names. Therefore, each of these subsources is plotted on the map in accordance with the modern town.

A detailed description of the Penn State Kaminaljuyu Project's Zone-Area-Sector system is necessary, since all geographic information for this study is dependent upon it. This system was developed for the settlement pattern study conducted throughout the Valley of Guatemala (Michels 1979b:5). It is based upon the series of 1:50,000 topographic maps developed by the Guatemalan Dirrection General de Cartografia that are oriented at grid north (Michels 1979b:5). Therefore, the Zone-Area-Sector system is also set at grid north. It is composed of three grids of varying resolution that fit within each other to create the integrated system. The first component of this system is the 'Zone', each of which has an area of 25 square kilometers. The next level of the grid is composed of 'Sectors', each encompassing 1 square kilometer. Finally, the highest resolution level of the system is made up of 'Areas', each containing 50 square meters. Therefore, coordinates within the system are listed in order of their zone, area, and sector. For example, there is an obsidian blade workshop at Kaminaljuyu located in Zone 46, Area 32, Sector 288. Therefore, its position can simply be referred to as "46-32-288", and its geographic provenience can be narrowed down to a specific 50 square meter 'sector' within the Valley of Guatemala. For this reason, any artifact or geological sample within a given Zone-Area-Sector can only be provenienced to an area of 50 square meters.



Figure 4.1 The Zone-Area-Sector System. From Michels 1979b:7.

The geographic information recorded by Hurtado de Mendoza for each sampled locality provided an early obstacle to correlating the sample with its location. Geographic data for each source that was sampled were recorded using the Kaminaljuyu Project's Zone-Area-Sector system (Michels 1979b:7), which was further built upon to cover a wider geographic range encompassing all sampled source localities. Coordinates were only recorded for the 'Zone' and 'Area' of each sampled geological locality, limiting geographic precision to 1 square kilometer. It was necessary to construct a GIS map so that the system could be georeferenced to modern coordinates. This permits the geographic provenience of the data to be associated with a universally accepted coordinate system. The Zone-Area-Sector system is only relevant to the Kaminaljuyu Project, and is not specific enough to facilitate replicable geographic information. Furthermore, the highest degree of accuracy is at the level of the "Sector" which encompasses 50 square meters. On the other hand, GPS coordinates provide a much more accurate measure of exact geographic location. Fortunately, GIS software provides the techniques to correlate the Zone-Area-Sector system with a universal coordinate system. Using maps from the reports of Michels and Hurtado de Mendoza, the Zone-Area-Sector system was able to be georeferenced onto a map with aerial and satellite imagery projected to a universal coordinate system. This proved to be a long, labor-intensive, and somewhat tedious process, but it provides a great degree of accuracy that can be coordinated with modern locational systems.

GIS Methodology

Data acquisition is perhaps one of the most time-consuming aspects of any GIS project. For this research, it was necessary to acquire data from a wide range of sources. For the purposes of referencing geographic information from the Kaminaljuyu Project with a present-day universally accepted coordinate system, various data were incorporated from a wide timeframe. All maps and Zone-Area-Sector coordinates from the Kaminaljuyu Project were scanned in from various publications by Michels (1979a, 1979b) and Hurtado de Mendoza (1977). This had to then be combined with present day aerial and satellite imagery, as well as elevation data. These data were acquired from a number of sources, including the United States Geological Survey's (USGS) Global Data Explorer and ESRI's data package that is made available with ArcGIS software.

The addition of these previously mentioned data provided a baseline from which the original Penn State project's Zone-Area-Sector grid system had to be georeferenced with universally available coordinates. This was done by correlating a mound in the center of the site

that was mapped by the project with its location in the modern Kaminaljuyu Archaeological Zone. The exact dimensions of the Zone-Area-Sector grid were replicated using the fishnet tool from a single mound that was used as a reference point. Specifically, the "Acropolis" of the site core was used as the point of reference (Michels 1979a:13). This is convenient, as it is located exactly at the northwestern corner of Zone 46, Area 23 (46-23). Since it is located in the presentday Parque Arqueologico Kaminaljuyu (Michels 1979b:6), the Acropolis was easily identifiable with satellite and aerial imagery.



Figure 4.2 Kaminaljuyu (within Zone 46). From Michels 1979a:13.



Figure 4.3 Location of the Kaminaljuyu Acropolis (46-23) within present day Guatemala City

Once Michels' grid system was georeferenced, it became possible to plot each of the sampled localities within the Valley of Guatemala into its respective sector. This provides one square kilometer of resolution, but given the available data from Hurtado de Mendoza's survey, it is impossible to provide any more precise geographic data. Nevertheless, the sampled localities are widely dispersed throughout the valley, and the resolution at which they have been plotted is sufficient for the purposes of this given study. Therefore, each of the sampled localities was digitized as point data in the GIS within their 1 sq. km. area. These points were generated as centroids of the 1 sq. km. area polygon that each sampled locality was associated with. The maximum margin of error for each point with respect to the actual geographic location of its sampled locality is just over .7 km (the square root of .5 km). This margin of error is simply calculated by using the Pythagorean Theorem to calculate the distance of each centroid point to any given corner of its 1 km. sq. area box (Figure 4.4). As long as this margin of error is accounted for, these points still provide the most accurate estimation of the location of each sampled source locality thus far. Furthermore, given the lack of detail of Hurtado de Mendoza's source survey, it is likely that these localities will never be plotted with any more accuracy until a more comprehensive source survey is conducted in the Valley of Guatemala and GPS coordinates are recorded for each sampling location.



Figure 4.4 Maximum Margin of Error for Geographic Provenience



Figure 4.5 The Zone-Area-Sector system georeferenced to modern satellite imagery of the Valley of Guatemala

Having confidently generated the above model of the Zone-Area-Sector system, it became possible to plot each sampled locality from Hurtado de Mendoza's source survey. This provides vital geographic information, as it permits geochemical subsource assignments to be given spatial reference. The methodology presented above provides a clear description of the steps that were taken to give accurate spatial information for each of the subsource groups that have been identified using geochemical techniques.



Figure 4.6 Georeferenced Source Sampling Localities

Chapter 5: Characterization of Subsources

pXRF Methodology

While it is necessary to describe the methodology completely for all types of analysis, this is particularly necessary for pXRF since the instrument can be run under a number of different settings, each of which may produce different results. Openly stating the decisions made about instrumentation, settings, and operating procedures make it easier to replicate results. This is basic scientific procedure not only for pXRF analysis, but also for all instrumental analysis (Speakman and Shackley 2013). Therefore care is taken in the discussion to explicitly outline all methodological decisions that were made for the present research.

Sample Selection

All source samples were selected from the materials used in Hurtado de Mendoza's (1977) dissertation research. In the summer of 1976, he conducted a source survey in the Valley of Guatemala to obtain samples from as many source localities as possible, as well as other localities of the Ixtepeque source system located near Guatemala's eastern border. All samples are from surface collections at the source (Hurtado de Mendoza 1977:10). After conducting his source survey, Hurtado de Mendoza stored all samples in envelopes labelled with their given name, locality number, and Zone-Area coordinates. Samples for pXRF analysis were selected from these materials that are presently stored at Penn State.

Selection of samples for pXRF analysis must meet a number of requirements so that accurate results can be obtained. The thickness and shape of each sample of obsidian must be considered so that the best results can be produced. Each sample must be optimally thick so that an accurate reading of the returning fluorescent rays is obtained (Ferguson 2012:413). Ideally, a sample should be at least 10 millimeters wide and 2 millimeters thick to ensure accurate results

(Shackley 2011:9). Samples with cortex were generally rejected as they contain uneven and dirty surfaces. Furthermore, it is necessary for each sample to have at least one facet that is flat and wide enough to cover the instrument's sensor. Each of these requirements was considered when selecting samples to analyze. Therefore, a number of samples that had been previously analyzed using neutron activation for Hurtado de Mendoza's research were not suitable for pXRF analysis. If a sample was not adequately thick or did not entirely cover the instrument's sensor, the measure of 'valid' counts of fluorescent rays read by the detector would decrease. This measure provides information about the number of X-rays that are returned from the sample that is being analyzed. Therefore, the higher the valid count, the more reliable the results will be. For this reason, these counts were monitored throughout the analysis. The sampling strategy for the present research analyzed as many samples for each source locality that met the dimensional requirements for pXRF. It should be expected that samples collected from the same location would return similar results. Therefore, analyzing multiple samples from each locality is ideal, since it ensures that the instrument is working properly and returning consistent results. This was not possible in the case of some sources for which dimensional requirements were not met, or if there were no available source samples at all in the Valley of Guatemala collections. Nevertheless, this study was able to analyze a large number of samples (n=215) from a wide variety of localities.

Upon selection, samples were removed and placed into a new bag with their source name, locality number, and Zone-Area coordinates. Furthermore, each sample was assigned a unique identification number for pXRF analysis. This identification consisted of an identification code of two or three characters for the sampled locality, along with a two digit sample number. For example, the "San Antonio North" locality is abbreviated as "SAN". Therefore, the first sample

from this locality was assigned the identification "SAN01", and the second sample was assigned "SAN02". This system enables the geochemical data for each sample to be easily associated with the exact sample from which it was obtained. Furthermore, it is easier to manage data files with Gauss statistical software and analyze source groups when each sample is organized through this system. Once samples were separated and assigned an ID number, their unique chemical compositions could be obtained through pXRF analysis.

Instrumentation

All samples were analyzed by energy-dispersive portable X-ray fluorescence using the Bruker Tracer III-V+ SD handheld XRF spectrometer. The instrument was equipped with a rhodium target X-ray tube and a 12 mil. Al, 1 mil. Ti, 6 mil. Cu (also known as 'green' or 'obsidian') filter. In order to convert incoming X-rays into characteristic energies and intensities, a silicon drift detector was used. This type of detector is known to obtain better count rates and resolution than Si(Li) detectors (Shackley 2011:32). The X-ray tube was operated at a voltage 40 kV, falling within the recommended 1.5-2 times absorption edge energy of the rhodium target tube (Shackley 2011:28), and a current of 24.8 μ A. All samples were analyzed for 200 seconds. At the beginning and end of each session of analysis, four known obsidian standards from sources outside of the study area were analyzed in order to ensure that the instrument was obtaining accurate, precise, and consistent readings throughout analysis. Furthermore, the temperature of the instrument and the 'valid counts' that were returned from each sample were monitored during analysis.

The instrument reads the peak energy intensities of each sample's elements and converts these to parts per million (ppm) values using a calibration from 40 obsidian standards provided by Bruker that have known elemental concentrations. The calibration was further enhanced by

removing individual concentrations that are not within the range of Mesoamerican obsidian. It is of the utmost importance to use the proper calibration when performing XRF analyses, since it ensures replicable data and accurate conversions of wavelengths into elemental concentrations expressed as parts-per-million values.

Operating Procedures

A number of steps must be taken to ensure accurate and replicable results. Prior to analysis, the instrument is placed on a stand so that X-rays are emitted upwards from the tube to the sample that is placed on top. Once powered on, the instrument must be connected to an input port on the computer, so that communication between the instrument and its computer software can occur. At this point, the settings by which analyses will occur can be set through the computer software. As previously discussed, these were set so that the instrument operated at 40 kV and 24.8 µA. Furthermore, the proper calibration file was selected at this point. Before analyzing samples, an initial 500 second run was conducted to warm-up the instrument. To begin analysis, each sample was placed directly on the instrument. Then, timed assays were set for 200 seconds. Throughout this run-time, the instrument's temperature and valid counts were monitored. Upon completing these steps, samples were removed from the instrument and placed back into their bag that is labelled with their assigned identification number.

Data Analysis

Elemental concentrations for each sample were immediately copied from the pXRF software to an Excel spreadsheet, where summary statistics for each sampled locality could be tabulated. Aside from this, the majority of all analysis was done using Gauss Runtime and MURRAP statistical routines v8.8c.

This software is freely available for download from the website of the University of Missouri Research Reactor's Archaeometry Laboratory, and it was recently updated to a newer version in May 2014 (Glascock 2014). This program was chosen since it is the most commonly used software to perform statistical analyses for archaeological geochemical provenance studies, since it provides all of the necessary tools for geochemical analyses. In order to make the original parts-per-million data compatible with the software, it was necessary to save each group sample as a Microsoft Excel 97 ".xls" file. The data were then imported into the program and converted to Gauss data ".dat" files. Once this was completed, a wide range of statistical analyses could be performed with the software. Prior to creating data groups from each sampled location, it was necessary to remove any outliers from the data. This eliminates statistical bias and is a suggested procedure by Glascock et al. (1998:25).

The main goal of the Gauss software is to identify as many geochemically distinct obsidian subsource groups as possible. First, it was necessary to group each sample according to its respective source system. Therefore, each sample was organized as a part of the El Chayal, San Martin Jilotepeque, or Ixtepeque source group. From here, a variety of statistical routines were performed to further identify subsource groups. While other geochemical studies have successfully used hierarchical cluster analysis to identify groups (Hurtado de Mendoza 1978; Braswell and Glascock 1998), the present study could not successfully make assignments solely using this method. Instead, bivariate plotting routines using various elemental concentrations proved to be the most effective way to distinguish groups. The remainder of this chapter will present the results of the geochemical analysis and provide maps for each of the obsidian subsource assignments that have been made at each sampling locality.

The Obsidian Source Systems of Highland Guatemala

This thesis geochemically characterizes three major source systems in Highland Guatemala: El Chayal (n=159), San Martin Jilotepeque (n=34), and Ixtepeque (n=22). The mean elemental concentrations and standard deviations for each source are listed in Table 5.1. The following results are from the pXRF analysis conducted as part of the present research.

Source System	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb	Sr/Zr	Rb/Zr	Y/Zr	Fe/Mn
(Sample Size)	(ppm)													
El Chayal	639	6777	35	17	10	138	141	19	104	9	1.357	1.329	0.188	10.846
(n=159)														
Standard	72	996	5	0	1	6	10	1	7	1	0	0	0	3
Deviations														
San Martin J.	579	7117	35	17	7	106	153	17	108	7	1.427	0.988	0.157	12.337
(n=34)														
Standard	50	1016	6	0	1	3	39	2	9	1	0	0	0	2
Deviations														
Ixtepeque	469	8847	28	17	7	93	140	18	150	9	0.935	0.621	0.121	19.077
(n=22)														
Standard	48	298	4	0	1	2	2	1	8	1	0	0	0	2
Deviations														

 Table 5.1 Mean elemental concentrations and standard deviations for El Chayal,

 San Martin Jilotepeque, and Ixtepeque source systems.

While differences can be observed in the concentrations above, bivariate plots provide an effective way to demonstrate how groups separate geochemically. To illustrate the differences between each of the Guatemalan sources, a plot of elemental concentrations in parts per million is shown below (Figure 5.1). Concentrations of rubidium (Rb) and iron (Fe) can be used to effectively discriminate obsidian source systems in Highland Guatemala.



Figure 5.1 Bivariate plot for concentrations of Rb (ppm) and Fe (ppm) for the El Chayal, San Martin Jilotepeque, and Ixtepeque source systems. Confidence ellipses drawn at .90

Three distinct groups can be seen in the plot above, and each is representative of a different obsidian source system. Probabilities of group membership for each sample have been calculated using Mahalanobis distnaces and are presented in Appendix C. Upon geochemically distinguishing each group, it is necessary to provide geographic context. The map below (Figure 5.2) shows the location of each sampling locality for the three major source systems.



Figure 5.2 Map of sampled source systems

The geochemical and geographic distinction of each of the source systems above demonstrates variation at a larger-scale source level. The goal of the present research is to examine variation **within** each of these sources by demonstrating geochemical and geographic variation at a much smaller scale. I refer to this as intrasource variation. The following sections will demonstrate intrasource variation for each of the systems examined by the present research.

Intrasource Variation at El Chayal

Subsource determinations were made for El Chayal from a total of 159 source specimens taken from 36 different sampling localities. Mean elemental concentrations and standard deviations for the five El Chayal subsources identified are presented below (Table 5.2).

Subsource	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb	Sr/Zr	Rb/Zr	Y/Zr	Fe/Mn
(Sample Size)	(ppm)													
El Chayal-1	541	8476	39	18	11	144	153	19	100	8	1.534	1.442	0.190	15.731
(n=17)														
Standard	33	507	4	0	1	3	4	1	2	0	0	0	0	1
Deviations														
El Chayal-2	667	6637	35	17	10	137	140	20	106	9	1.318	1.296	0.187	10.015
(n=113)														
Standard	47	751	4	0	1	4	8	1	3	1	0	0	0	1
Deviations														
El Chayal-3	633	5463	33	17	10	138	129	20	89	8	1.447	1.553	0.220	8.686
(n=16)														
Standard	43	380	4	0	1	5	6	2	3	1	0	0	0	1
Deviations														
El Chayal-4	488	7198	27	17	10	128	151	17	113	9	1.335	1.139	0.148	15.064
(n=10)														
Standard	73	420	4	0	1	5	8	1	4	1	0	0	0	2
Deviations														
El Chayal-5	674	8034	38	18	11	156	166	22	117	10	1.423	1.334	0.186	11.940
(n=3)														
Standard	22	228	4	0	0	3	5	1	2	1	0	0	0	1
Deviations														

Table 5.2 Mean elemental concentrations for El Chayal subsources (n=159)

Table 5.2 demonstrates that specific elemental concentrations can be used to distinguish subsource groups for the El Chayal source system. Variation is seen in concentrations of Manganese (Mn), Iron (Fe), Rubidium (Rb), Strontium (Sr), and Zirconium (Zr). The bivariate plot (Figure 5.3) shows subsource variation at El Chayal using concentrations of Zirconium (Zr) and Rubidium (Rb). Five distinct geochemical groups are observed within the El Chayal obsidian source.



Figure 5.3 Bivariate plot for concentrations of Zr (ppm) and Rb (ppm) for El Chaval subsources. Confidence ellipses drawn at .90

While there are some outliers, the groups discriminate well both geochemically and geographically. Mahalanobis distance group membership probabilities for each sample are provided in Appendix C (although data are unavailable for El Chayal-4 and El Chayal-5 as a result of sample size restrictions). The geographic distribution of each of the El Chayal subsources are mapped in Figure 5.4.



Figure 5.4 Map of El Chayal subsource assignments

Each of the subsource groups cluster geographically. El Chayal-1 is located at the far eastern end of the source system, while El Chayal-2, the largest subsource, is clustered around the El Chayal Chipping Station. El Chayal-3 is located to the east around the town of San Antonio. El Chayal-4 clusters just south of El Chayal-2. El Chayal-5 is located just north of Guatemala City. This spatial variation is significant as it shows that different geochemical signatures from unique subsources can be used effectively to determine geographic provenience at higher levels of precision The combination of geochemical techniques with GIS have permitted distinct subsources of the El Chayal obsidian source system to be identified and mapped on the landscape of the Valley of Guatemala.

Intrasource Variation at San Martin Jilotepeque

Subsource determinations were made for San Martin Jilotepeque with a total of 34 source specimens from 8 sampling localities. Mean elemental concentrations and standard deviations for the two San Martin Jilotepeque subsources identified are presented below (Table 5.3).

Subsource	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb	Sr/Zr	Rb/Zr	Y/Zr	Fe/Mn
(Sample Size)	(ppm)													
SMJ-1 (n=30)	582	6842	36	17	7	106	167	17	108	7	1.561	0.991	0.154	11.778
Standard Deviations	47	618	6	0	1	3	8	2	10	1	0	0	0	1
SMJ-2 (n=4)	561	9183	32	17	8	107	48	20	112	5	0.427	0.962	0.184	16.529
Standard Deviations	68	1038	3	0	1	3	3	1	4	1	0	0	0	2

Table 5.3 Mean elemental concentrations and standard deviations for San Martin Jilotepeque subsources (n=34)

Similar elemental concentrations can be used to distinguish subsource groups for the San Martin Jilotepeque source system. Variation is particularly seen in concentrations of Manganese (Mn), Iron (Fe), Rubidium (Rb), Strontium (Sr), and Zirconium (Zr). Figure 5.5 demonstrates subsource variation at San Martin Jilotepeque using concentrations of Strontium (Sr) and Rubidium (Rb).



Figure 5.5 Bivariate plot for concentrations of Sr (ppm) and Rb (ppm) for San Martin Jilotepeque subsources. Confidence ellipses drawn at .90

Two distinct geochemical groups were found within the San Martin Jilotepeque obsidian source (Figure 5.5). Despite the total sample size being smaller than El Chayal, the groups discriminate well both geochemically and spatially. Mahalanobis distance group membership probabilities for each sample are provided in Appendix C (data unavailable for SMJ-2 as a result of small sample size). Figure 5.6 illustrates the geographic distribution of each of the San Martin Jilotepeque subsources, providing geographic provenience for the distinct subsource groups that have been identified.



Figure 5.6 Map of San Martin Jilotepeque subsource assignments

As can be seen in Figure 5.6, the two subsource groups cluster geographically. Similar to El Chayal, this is significant as it demonstrates that geochemical signatures can be used to determine geographic provenience with more spatial precision. While the SMJ-1 subsource is generally concentrated in the northern portion of the source area, SMJ-2 clusters at the southern end. The combination of pXRF analysis and GIS provides evidence of geochemical and spatial variation within the San Martin Jilotepeque obsidian source system.

Intrasource Variation at Ixtepeque

Subsource determinations were made for Ixtepeque with a total of 22 source specimens from 4 sampling localities. Mean elemental concentrations and standard deviations for the two Ixtepeque subsources that have been identified are presented below (Table 5.3).

Subsource	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb	Sr/Zr	Rb/Zr	Y/Zr	Fe/Mn
(Sample Size)	(ppm)													
IXT-1 (n=17)	449	8979	27	17	7	93	140	18	154	9	0.907	0.606	0.117	20.067
Standard Deviations	29	189	4	0	1	2	2	1	2	1	0	0	0	1
IXT-2 (n=5)	537	8396	31	17	6	91	139	18	135	9	1.031	0.671	0.134	15.711
Standard Deviations	35	79	2	0	1	2	2	0	0	0	0	0	0	1

Table 5.4 Mean elemental concentrations for Ixtepeque subsources (n=22)

Table 5.4 demonstrates that some specific elemental concentrations can be used to distinguish subsource groups for the Ixtepeque source system. As with El Chayal and San Martin Jilotepeque, samples vary in concentrations of Manganese (Mn), Iron (Fe), Rubidium (Rb), Strontium (Sr), and Zirconium (Zr). Figure 5.7 demonstrates subsource variation at Ixtepeque using concentrations of Zirconium (Zr) and Strontium (Sr).



Figure 5.7 Bivariate plot of concentrations of Zr (ppm) and Sr (ppm) for Ixtepeque subsources. Confidence ellipses drawn at .90

Two distinct geochemical groups are seen within the Ixtepeque source. Despite the total sample size being smaller than those of the El Chayal and San Martin Jilotepeque source groups, the samples discriminate well both geochemically and spatially. Mahalanobis distance group membership probabilities for each sample are provided in Appendix C (data unavailable for IXT-2 as a result of sample size constraints). Figure 5.8 illustrates the geographic distribution of the Ixtepeque subsources. This provides geographic provenience for the distinct subsource groups that have been identified.



Figure 5.8 Map of Ixtepeque Subsource Assignments

Figure 5.8 confirms that two subsource groups are spatially discrete. The IXT-1 subsource is located in the southern portion of the source near the small town of Papalhuapa as well as towards the west at the Las Animas quarry at the foot of the Ixtepeque volcano. IXT-2 clusters at the northern end near the town of Agua Blanca. The combination of pXRF analysis and GIS provides evidence of geochemical and spatial variation within the Ixtepeque obsidian source system.

Chapter 6: Discussion

The combination of pXRF analysis with GIS mapping techniques has demonstrated the geochemical and spatial variation within three different obsidian sources in Highland Guatemala. The identification of different subsources within each of these areas has many archaeological implications. This chapter will discuss the data presented for each of the obsidian subsources examined by this thesis and their implications for archaeological research.

The El Chayal Subsources

This research has identified five distinct subsources of the El Chayal obsidian source system by geochemically characterizing 159 samples from 36 different source localities. The majority of the subsource groups identified are spatially discrete. A few exceptions to this are seen with the El Chayal-2 subsource, for which there are some outliers that overlap geographically with other subsource areas. While it is possible that this could be the result of overlapping volcanic flows, it is the author's opinion that these outliers are the result of either "float" source samples or inconsistencies in the source sampling survey. All issues concerning outliers such as these will be further discussed later in this chapter.

The subsource identifications for El Chayal presented here improve upon previous research in several ways. Primarily, accurate geographic provenience is provided for each subsource. Previous research by Hurtado de Mendoza (1978) failed to provide spatial information for subsources. Secondly, the total number of samples analyzed is increased, and data for each sample is presented in the appendices. Hurtado de Mendoza analyzed a smaller sample of El Chayal obsidian (he does not specify the sample size specific to El Chayal, but his entire sample of El Chayal, San Martin Jilotepeque, and Ixtepeque consisted of 179 specimens).

The present research uses a total of 215 samples and provides all raw data and totals for each sampled locality. Finally, this research uses new techniques. While Hurtado de Mendoza simply made groups through hierarchical cluster analysis of iron and manganese concentrations, this project considered concentrations for ten different elements and uses improved statistical techniques to define groups. The data presented here are in accordance with the work of Hurtado de Mendoza, since he identifies five distinct groups at El Chayal as well.

The identification of El Chayal subsources is significant for archaeological research not only in the Valley of Guatemala but also for Mesoamerica as a whole. El Chayal was one of the most important and widely exploited obsidian sources in ancient Mesoamerica. Most raw materials for large-scale blade production were quarried at the El Chayal Chipping Station; therefore, the majority of El Chayal obsidian throughout Mesoamerica may be expected to come from the El Chayal-2 subsource. Unfortunately, no provenience studies have been done to characterize El Chayal obsidian at the subsource level. The identification of different subsource exploitation at El Chayal could have great implications about the obsidian procurement, production, and distribution systems that operated at different times in Mesoamerican prehistory. The data presented for El Chayal subsources could be used not only for research within the Valley of Guatemala, but could also be used to identify procurement systems at a larger geographic scale.

The San Martin Jilotepeque Subsources

Two San Martin Jilotepeque subsources have been identified by analyzing 34 source specimens from 8 sampling localities. While the identification of two chemically and spatially distinct groups is an important addition to the available data pool for San Martin Jilotepeque

obsidian characterization, the sample used for this project is not comprehensive enough to make any sweeping contributions to our understanding of subsources of San Martin Jilotepeque. Fortunately, Braswell and Glascock (1998) have already published a comprehensive subsource characterization study for this source system. A comparison of this the present results for San Martin Jilotepeque and those of Braswell and Glascock (1998) provides one interesting discrepancy that should be addressed by future research. While elemental concentrations for the subsource SMJ-1 are similar to Braswell and Glascock's data, SMJ-2 has notably low concentrations of strontium with an average of 48 ppm. No subsources have previously been identified at the San Martin Jilotepeque source system with strontium concentrations such as this. Although the sample size for SMJ-2 is small (n=4), all data are within three standard deviations of the mean. Furthermore, both localities for SMJ-2 cluster geographically at the southern end of the source system. While it is possible that SMJ-2 is a new addition to the pool of San Martin Jilotepeque subsources that have been identified, not much can be confidently said without conducting a more comprehensive survey of the area.

The Ixtepeque Subsources

Two Ixtepeque subsources have been identified from an analysis of 22 source specimens from 4 sampling localities. Both groups are geochemically and spatially discrete. While the sample is small, the data presented for Ixtepeque are the first subsource characterizations available for the source. It is likely that more unique subsources could be identified at Ixtepeque with a comprehensive survey of the source. The data presented for Ixtepeque provide a baseline for future source research.

pXRF and Subsource Characterization in Highland Guatemala

This research is both an important contribution to our understanding of obsidian subsources and it is significant methodologically. The subsource characterizations provided confirm that portable X-ray fluorescence can be used to accurately and efficiently characterize obsidian subsources. Furthermore, it is particularly useful in Highland Guatemala where sources often display the most variation for their concentrations of heavy elements such as Strontium, Rubidium, and Zirconium. Nevertheless, some inconsistencies were encountered throughout the course of this research.

Inconsistent Results

Several of the inconsistencies observed among the data must be addressed by further research. Theoretically, every piece of obsidian from a single sampled locality should have consistent geochemical properties. This is expected of obsidian, since it is chemically homogenous within each source and sub-source. Nevertheless, a small percentage of the samples analyzed produced inconsistent results within their sampled localities. This only occurred within a locality as a single outliers within a larger sample. While it is possible that some of these outliers could be a result of methodological inconsistencies or problems with the sample, there is also a possibility that varying results within a sampled locality are the result of anthropogenic processes. It is necessary to consider all possibilities to best understand why some results of pXRF geochemical analysis do not adhere to their expectations.

As described in earlier chapters, a number of possible methodological issues with the pXRF instrument could contribute to inconsistencies in the data. However, these factors were controlled throughout this research, and it is unlikely that they had any influence on the results.
Potential problems with the sample itself could also lead to inconsistent results. A number of these issues have already been addressed in the discussion of sample selection in Chapter 5.

Since problems with instrumentation and sampling were controlled for, it is likely that inconsistencies in the data should be attributed to other factors. The best explanation is "drift" (Hurtado de Mendoza 1977:59) or 'float' processes at the localities that were sampled. This term refers to the occurrence of obsidian in a place other than the original flow from which it came. Hurtado de Mendoza (1977:59) explains that this can occur by two different modes of transportation: "natural" and "cultural" drift.

Natural drift processes refer to environmental variables such as erosion and alluvial flows that could possibly displace material from its original spot on the landscape. Hurtado de Mendoza provides the example of samples from the Cruz de Apan source system that most likely experienced natural drift. In the case of this sampling locality, obsidian likely drifted from its original deposit downstream via the Agua Caliente creek (Hurtado de Mendoza 1977:60).

Cultural drift encompasses any prehistoric or modern human interference that led to the presence of obsidian at a spot other than its original source. A simple way that this could occur either prehistorically or more recently is by simple human transportation. It is very plausible that humans in the past or present could simply pick up raw materials at the source and deposit them elsewhere. Hurtado de Mendoza (1977:61) also provides a more complicated modern scenario of a cultural drift process. Modern road cuts and tunneling for various public works often uncover obsidian deposits that were too deeply buried for exploitation in the past. Once these deposits are uncovered, they can be distributed to other localities via cultural drift processes by which humans remove obsidian from its original source and deposit it elsewhere. The influence that

cultural drift processes could have on the results of geochemical sourcing techniques should not be underestimated.

A number of confounding influences that could lead to unexpected results have been considered. Archaeologists must be aware of the problems that can arise when analysis is performed with methodological consistencies. This was very carefully considered for the present research. Therefore, it is very unlikely that practices such as this influenced the results. Issues with the sample itself are another possible influence on the results obtained using pXRF analysis. Once again, great care was taken to avoid any such problems. Finally, it is important to understand the various drift processes by which obsidian can occur at a location other than its original source. This happens either by natural or cultural influences, but is a reality that must be considered when collecting obsidian source samples. It is likely that any inconsistent data within each sampled locality for the present research are the result of processes such as this. Unfortunately, this issue is best controlled while collecting source samples at each locality. It is likely that Hurtado de Mendoza simply collected loose pieces of obsidian that appeared to be raw material at each of the localities that were sampled. His sampling strategy would have been more efficient if he took care to only sample obsidian when it clearly was part of a natural deposit. This can be done by taking flakes from large, immovable nodules at the source locality. This kind of collection strategy would provide greater certainty that each source sample had not previously undergone any natural or cultural drift processes. Although the majority of the data from the present research are consistent within each sampled locality, future research could benefit from a stricter sampling strategy.

Conclusion

The present research successfully characterized obsidian subsources at the highland Guatemalan source areas of El Chayal, San Martin Jilotepeque, and Ixtepeque. A combination of pXRF spectrometry and GIS mapping identified each subsource as a geochemically and spatially distinct unit. Using samples collected as part of Penn State's Kaminaljuyu Project during the 1970's, five distinct subsources were identified at El Chayal. Furthermore, two unique subsources were identified at both San Martin Jilotepeque and Ixtepeque. This thesis presents the geochemical and geographic data that have been used to make these distinctions.

This research has also demonstrated that pXRF enables archaeologists to geochemically characterize obsidian both efficiently and accurately. Although some problems have been encountered with the original source survey, the combination of geochemical techniques with GIS technology enables subsource groups to be accurately determined. This thesis proposes that future research can rely on pXRF spectrometry combined with a systematic source survey to confidently characterize obsidian in Mesoamerica.

The data presented in this thesis serves as a baseline for future archaeological work. The subsources identified demonstrate the chemical and spatial variation that should be expected within obsidian sources in Highland Guatemala. Subsource characterization at all Highland Guatemalan sources would benefit from a more comprehensive source survey with systematic sampling and geographic coordinates. With the flexibility permitted by technology such as Portable XRF technology and GPS units, a survey could be conducted with high levels of accuracy and efficiency. Furthermore, a number of obsidian provenance studies are facilitated at small and larger scales using the subsource data provided. The identification of different

subsources exploited across geographic space and time will have many implications about how obsidian industry systems operated in pre-Hispanic Mesoamerica. The data presented for this thesis creates the opportunity for a great deal of archaeological research in the future.

Appendix A: Concentrations for All Samples

El Chayal

Anid	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb	Source	Subsource
LJT01	476	8162	33	17	11	146	154	20	100	9	El Chayal	1
LJT02	486	8799	45	18	11	151	158	20	104	8	El Chayal	1
LJT03	545	8309	36	17	10	140	151	19	101	9	El Chayal	1
LJT04	571	9921	37	18	11	140	148	18	100	8	El Chayal	1
LJT05	541	7995	36	17	10	141	150	19	100	8	El Chayal	1
LJT06	545	9609	42	18	14	146	156	18	98	8	El Chayal	1
LJT07	565	8271	39	18	11	141	151	19	100	8	El Chayal	1
LJT08	533	8315	37	18	10	145	150	18	101	8	El Chayal	1
LJT09	552	8228	33	18	12	141	151	18	98	7	El Chayal	1
LJT10	512	8290	50	18	10	139	153	19	98	8	El Chayal	1
LMZ01	547	8127	45	18	11	143	153	19	100	8	El Chayal	1
LMZ02	513	8162	35	18	12	142	145	19	99	7	El Chayal	1
LMZ03	501	8495	40	18	11	145	157	19	98	8	El Chayal	1
LMZ04	563	8533	38	18	11	149	160	18	101	9	El Chayal	1
LMZ05	599	8112	41	18	11	141	149	19	96	8	El Chayal	1
LMZ06	560	8364	37	17	11	146	155	19	99	8	El Chayal	1
LMZ08	583	8399	40	18	11	145	155	19	99	8	El Chayal	1
CH01	651	5844	30	17	9	137	133	17	101	9	El Chayal	2
CH02	712	6075	32	17	10	140	139	20	105	9	El Chayal	2
CH03	687	5943	33	17	10	138	138	20	106	10	El Chayal	2
CH04	662	6009	34	17	9	136	135	19	105	9	El Chayal	2
CH05	680	6029	37	18	10	136	139	21	107	9	El Chayal	2
CH06	656	6084	34	17	12	140	140	19	106	9	El Chayal	2
CH07	679	6115	33	17	10	137	138	18	106	10	El Chayal	2
CH08	667	5994	30	17	9	135	137	19	108	10	El Chayal	2
CH09	656	6042	33	17	10	138	134	19	105	9	El Chayal	2
CH10	617	6155	34	17	10	139	140	20	103	10	El Chayal	2
CH11	662	5925	27	17	9	137	135	20	104	11	El Chayal	2
CH12	705	6177	33	17	11	142	131	19	106	8	El Chayal	2
CCH01	624	6086	34	17	12	143	140	20	107	9	El Chayal	2
CCH02	719	6729	46	18	10	144	143	19	109	10	El Chayal	2
CCH03	713	6296	37	17	9	134	136	20	106	8	El Chayal	2
EF01	706	5963	39	17	9	131	130	21	101	8	El Chayal	2
K2401	666	6017	37	17	8	126	127	20	102	7	El Chayal	2
BV01	670	6405	40	17	9	140	139	21	105	9	El Chayal	2
LV01	659	6125	32	17	9	142	143	20	106	11	El Chayal	2
LV02	650	6121	32	17	11	144	146	23	108	11	El Chayal	2
LV03	610	6295	43	18	10	135	135	20	103	9	El Chayal	2

LV04	698	6127	33	17	11	134	132	20	105	7	El Chayal	2
LV05	662	6254	39	18	11	141	136	20	109	9	El Chayal	2
AC07	682	6237	36	17	9	134	132	20	106	9	El Chayal	2
AC08	739	6294	35	17	10	140	139	20	108	9	El Chayal	2
AC09	703	6460	34	17	10	138	132	19	106	7	El Chayal	2
AC10	651	6217	33	17	9	130	128	18	102	9	El Chayal	2
AC11	691	7248	43	18	9	134	134	18	100	9	El Chayal	2
AC12	664	6407	34	17	8	130	127	20	100	8	El Chayal	2
AC13	516	6675	29	17	10	129	125	18	103	7	El Chayal	2
AC14	713	6235	35	17	10	135	127	18	104	8	El Chayal	2
AC15	724	6240	38	17	8	132	128	20	103	8	El Chayal	2
AC16	650	6504	34	17	11	133	129	20	105	9	El Chayal	2
K2501	717	6526	39	17	9	134	131	19	105	7	El Chayal	2
AZ01	763	7394	43	18	12	145	143	22	111	11	El Chayal	2
AZR01	648	6197	31	17	10	137	136	21	105	10	El Chayal	2
AZR02	605	6276	33	17	10	138	137	20	107	10	El Chayal	2
AZR03	706	5906	37	18	11	139	137	18	105	9	El Chayal	2
AZ05	695	6415	35	17	9	137	139	20	106	9	El Chayal	2
KM01	597	6999	37	18	11	141	149	19	107	9	El Chayal	2
KM02	712	7243	31	17	10	141	153	21	111	9	El Chayal	2
KM03	669	8248	32	17	10	147	154	20	109	10	El Chayal	2
KM04	619	8341	38	18	11	141	144	21	108	7	El Chayal	2
RU01	709	6786	35	17	10	139	137	20	102	10	El Chayal	2
RU02	655	7399	40	18	12	144	156	21	110	10	El Chayal	2
RU03	558	7636	34	17	10	138	149	20	104	9	El Chayal	2
RU04	678	8421	38	18	11	138	141	20	105	9	El Chayal	2
LVP02	661	7360	35	18	11	142	154	21	111	9	El Chayal	2
LVP03	530	7055	30	17	12	139	146	20	108	9	El Chayal	2
LVP04	660	7067	34	17	11	144	152	21	108	9	El Chayal	2
LVP05	571	6656	39	18	11	132	142	21	104	8	El Chayal	2
LVP06	661	7343	32	17	8	139	149	21	109	8	El Chayal	2
PA01	629	6306	42	18	11	141	140	20	107	11	El Chayal	2
PA02	674	5977	36	17	10	139	136	20	106	10	El Chayal	2
PA03	691	6122	40	18	11	138	134	19	106	9	El Chayal	2
PA04	619	6323	43	18	8	133	133	18	101	8	El Chayal	2
MO01	702	6217	37	18	12	142	148	21	109	11	El Chayal	2
MO02	704	7402	46	18	10	142	137	21	106	9	El Chayal	2
MO03	668	6575	43	18	8	128	138	20	106	9	El Chayal	2
PG01	683	6267	38	17	9	135	140	20	104	10	El Chayal	2
PG02	696	6551	37	18	9	139	145	18	109	9	El Chayal	2
PG03	667	6404	43	18	9	139	145	21	112	8	El Chayal	2
PG04	724	7299	41	18	10	142	144	18	108	8	El Chayal	2
PG05	684	8186	41	18	10	144	150	19	110	9	El Chayal	2
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LP01	682	7098	35	18	12	146	139	21	109	10	El Chayal	2
LP02	612	6773	38	17	7	129	127	19	104	7	El Chayal	2
LP03	641	6878	31	17	8	130	126	18	100	8	El Chayal	2
LP04	635	6662	32	17	10	129	128	19	102	9	El Chayal	2
LP05	699	6734	38	17	9	139	138	20	105	9	El Chayal	2
SJG03	718	6768	39	18	11	144	153	21	108	9	El Chayal	2
EP01	679	6056	35	17	11	137	139	19	107	10	El Chayal	2
EP02	616	6175	31	17	9	137	138	21	112	10	El Chayal	2
EP03	716	6196	38	17	9	140	140	19	111	8	El Chayal	2
EP04	750	6676	40	18	10	141	145	19	114	8	El Chayal	2
EP05	643	10472	45	18	9	133	133	19	107	9	El Chayal	2
HN01	626	6082	37	17	10	138	136	20	106	10	El Chaval	2
AT01	663	6215	42	18	10	140	135	20	110	10	El Chayal	2
AT09	714	7072	31	17	10	135	137	19	106	8	El Chayal	2
AT10	647	5981	32	17	9	135	136	19	104	8	El Chayal	2
AT11	731	6066	29	17	8	134	131	20	104	9	El Chayal	2
EP101	624	7147	31	17	8	133	151	20	105	8	El Chayal	2
EP102	673	7145	30	17	8	138	157	19	105	9	El Chayal	2
EP103	642	6893	32	17	9	130	137	19	101	7	El Chayal	2
EP104	688	6927	25	17	8	133	141	20	107	7	El Chayal	2
EP105	710	6592	36	17	9	135	135	21	102	8	El Chayal	2
EP106	705	6177	33	17	9	136	132	19	104	7	El Chayal	2
EP107	602	7735	31	17	8	133	150	19	104	7	El Chaval	2
EP108	696	7017	34	17	8	135	144	20	109	8	El Chaval	2
EP109	584	7578	39	18	11	142	151	22	109	8	El Chayal	2
EP110	591	7093	38	18	9	137	148	20	103	8	El Chaval	2
EP201	667	7169	28	17	11	140	162	21	109	10	El Chaval	2
EP202	631	7066	37	17	10	138	147	22	106	9	El Chaval	2
EP203	674	7139	37	17	9	135	146	19	104	9	El Chaval	2
EP204	646	7021	32	17	12	138	152	19	107	8	El Chaval	2
EP205	592	6904	32	17	9	136	154	20	105	7	El Chaval	2
EP206	643	7348	36	17	9	142	156	20	109	8	El Chaval	2
EP208	657	7261	30	17	9	136	150	20	104	8	El Chaval	2
EP209	777	9679	31	17	9	135	141	20	108	8	El Chaval	2
EP210	595	7170	43	18	10	137	158	19	106	9	El Chaval	2
01001	702	6500	34	17	11	137	136	19	106	9	El Chaval	2
01002	574	6049	34	17	9	132	132	20	103	10	El Chaval	2
01003	670	6183	35	17	9	137	137	20	105	10	El Chaval	2
01004	712	6228	33	17	10	140	139	18	107	10	El Chaval	2
01005	667	6391	39	17	8	137	134	20	106	9	El Chaval	2
25401	724	5833	33	17	10	136	132	19	107	10	El Chaval	2
25402	690	6063	33	17	9	143	139	18	105	9	El Chaval	2
25403	693	6005	31	17	9	137	136	19	106	11	El Chaval	2
25404	651	5918	32	17	9	133	131	20	103	9	El Chaval	2
25405	573	6002	35	18	12	137	137	20	106	11	El Chaval	2
25406	685	5652	33	17	10	133	134	19	101	8	El Chaval	2
25407	701	6017	29	17	11	135	132	20	105	9	El Chaval	2
		0017		- '		100			100		2. Chajai	

25409	705	6053	35	17	10	140	139	19	108	11	El Chaval	2
25410	717	5860	39	17	8	133	135	18	102	7	El Chayal	2
SLP01	674	5233	34	17	9	134	123	18	88	7	El Chayal	3
SAN01	645	5408	27	17	10	141	130	23	92	8	El Chayal	3
SAN03	615	5505	36	18	12	147	127	21	90	9	El Chayal	3
SAN04	667	5440	30	17	9	140	127	20	88	8	El Chayal	3
SAS04	579	4955	28	17	8	132	123	18	88	9	El Chayal	3
SAS07	598	5389	35	17	11	140	136	20	90	9	El Chayal	3
SAS10	717	5444	35	17	8	137	129	18	89	8	El Chayal	3
ER02	642	5374	37	17	10	140	122	20	87	8	El Chayal	3
EC01	617	5063	30	17	10	140	126	19	86	9	El Chayal	3
EC02	639	5210	37	17	10	143	125	19	84	8	El Chayal	3
EC03	592	5226	33	17	9	134	122	19	86	8	El Chayal	3
SRE01	527	6546	23	17	12	126	148	17	92	9	El Chayal	3
23701	654	5258	37	17	9	137	129	19	86	7	El Chayal	3
23702	655	5589	35	17	10	135	129	17	94	7	El Chayal	3
23704	652	6120	34	17	9	141	130	21	92	7	El Chayal	3
23705	656	5652	36	17	8	139	132	21	90	8	El Chayal	3
RC02	462	7372	24	17	11	129	153	16	114	8	El Chayal	4
RC04	519	7127	20	17	9	124	154	17	115	9	El Chayal	4
RC05	494	7622	27	17	9	129	157	17	118	9	El Chayal	4
RC06	471	7135	34	17	11	125	150	15	113	7	El Chayal	4
LM01	428	6998	29	17	11	131	156	17	114	9	El Chayal	4
LM02	418	6759	26	17	8	123	147	16	112	9	El Chayal	4
LM03	460	7037	24	17	10	122	145	18	108	8	El Chayal	4
LM04	428	7814	27	17	10	137	159	17	117	9	El Chayal	4
LM05	518	7714	25	17	11	133	153	15	113	9	El Chayal	4
LM13	680	6399	31	17	8	132	132	18	105	9	El Chayal	4
LJ01	703	7829	36	18	11	159	165	22	120	12	El Chayal	5
LJ02	668	7920	35	18	12	152	161	20	116	10	El Chayal	5
LJ03	651	8352	43	18	12	157	172	23	115	9	El Chayal	5
Average	639	6777	35	17	10	138	141	19	104	9		
STD DEV	72	996	5	0	1	6	10	1	7	1		
%rsd	11	15	14	1	12	4	7	7	6	12		

San Martin Jilotepeque

Anid	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb	Source	Subsource
APO06	543	6439	38	17	5	100	165	17	101	6	Jilotepeque	1
APO07	630	6706	32	17	7	105	167	16	106	7	Jilotepeque	1
APO09	586	6708	36	17	7	109	170	17	103	8	Jilotepeque	1
APO10	602	6447	31	17	8	105	161	15	103	7	Jilotepeque	1
PX01	640	7577	43	17	6	107	148	22	135	9	Jilotepeque	1
PX02	516	6294	30	17	7	108	166	16	102	6	Jilotepeque	1
PX03	616	7588	55	18	7	107	151	19	140	10	Jilotepeque	1
PX04	510	6213	37	17	6	102	161	15	100	7	Jilotepeque	1
PX05	580	6383	43	18	8	106	166	16	105	6	Jilotepeque	1
PX06	567	7556	46	17	6	104	168	17	103	7	Jilotepeque	1
PX07	626	6436	33	17	7	108	169	16	103	8	Jilotepeque	1
PX08	586	6606	30	17	7	107	170	15	106	7	Jilotepeque	1
PX09	560	6177	32	17	7	105	164	15	102	8	Jilotepeque	1
PX10	599	6858	35	17	8	112	181	16	111	7	Jilotepeque	1
QM01	533	6442	32	17	7	105	163	14	102	7	Jilotepeque	1
QM02	589	6307	38	17	6	103	172	16	100	7	Jilotepeque	1
QM03	551	6562	32	17	7	104	162	15	100	7	Jilotepeque	1
QM04	524	6718	33	17	9	109	168	16	104	7	Jilotepeque	1
QM05	567	7784	34	17	9	105	171	18	106	6	Jilotepeque	1
QM06	550	6541	32	17	7	106	163	15	101	8	Jilotepeque	1
QM07	578	6428	32	17	8	106	164	16	103	6	Jilotepeque	1
QM08	565	6458	26	17	8	106	170	17	106	8	Jilotepeque	1
QM09	617	7355	38	17	9	112	180	17	108	7	Jilotepeque	1
QM10	618	6860	40	17	6	109	180	19	108	7	Jilotepeque	1
DP01	513	6613	32	17	8	106	174	16	107	7	Jilotepeque	1
ERO01	564	6718	31	17	8	104	168	16	107	6	Jilotepeque	1
SMJ06	592	7177	40	17	6	97	150	18	113	6	Jilotepeque	1
SMJ07	641	8012	28	17	6	105	162	17	117	7	Jilotepeque	1
SMJ08	552	6422	36	17	8	111	174	17	107	7	Jilotepeque	1
SMJ09	738	8865	41	17	8	113	181	19	129	8	Jilotepeque	1
FP01	653	8561	30	17	6	103	43	20	110	5	Jilotepeque	2
SAI01	491	8191	33	17	9	108	48	20	108	6	Jilotepeque	2
SAI03	500	9085	31	17	8	107	49	21	111	6	Jilotepeque	2
SAI04	600	10894	36	17	8	112	51	21	118	5	Jilotepeque	2
Average	579	7117	35	17	7	106	153	17	108	7		
STD DEV	50	1016	6	0	1	3	39	2	9	1		
%rsd	9	14	16	1	14	3	26	11	9	15		
				1	A.4		-0	* *		10	1	

Ixtepeque

Anid	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb	Source	Subsource
LA01	464	8757	27	17	6	89	134	17	150	9	Ixtepeque	1
LA02	468	9190	33	17	7	95	143	18	156	9	Ixtepeque	1
LA03	397	8792	28	17	6	94	139	18	153	9	Ixtepeque	1
LA04	480	9206	24	17	8	94	142	18	157	9	Ixtepeque	1
LA05	418	8612	28	17	6	91	138	17	150	8	Ixtepeque	1
LA06	502	8853	26	17	7	94	145	17	156	10	Ixtepeque	1
LA07	480	9142	24	17	8	97	143	19	158	8	Ixtepeque	1
LA08	429	9292	23	17	7	93	139	20	153	9	Ixtepeque	1
LA09	404	8978	31	17	6	94	139	17	152	11	Ixtepeque	1
LA10	426	8800	24	17	8	93	140	18	154	9	Ixtepeque	1
LA11	447	9035	18	17	7	91	140	19	156	11	Ixtepeque	1
LA12	449	8928	29	17	5	92	139	18	157	9	Ixtepeque	1
PH01	437	9100	24	17	6	97	140	18	154	8	Ixtepeque	1
PH02	474	8975	25	17	7	95	141	18	156	9	Ixtepeque	1
PH03	421	8764	27	17	6	93	139	18	153	8	Ixtepeque	1
PH04	464	9009	25	17	7	95	142	19	157	10	Ixtepeque	1
OA01	475	9215	36	17	6	93	138	18	153	8	Ixtepeque	1
AB01	555	8311	32	17	5	91	140	17	135	9	Ixtepeque	2
AB03	555	8374	32	17	6	89	136	18	135	9	Ixtepeque	2
AB04	537	8476	33	17	6	94	139	18	134	10	Ixtepeque	2
CD01	470	8318	28	17	7	91	138	18	135	9	Ixtepeque	2
CD02	566	8500	29	17	7	89	142	19	135	9	Ixtepeque	2
Average	469	8847	28	17	7	93	140	18	150	9		
STD DEV	48	298	4	0	1	2	2	1	8	1		
%rsd	10	3	15	1	11	3	2	4	6	8		

Z-A-S	Name	Assignment	Code
265-22	La Joyita	El Chayal-1	LJT
265-22	Los Mezcales	El Chayal-1	LMZ
11-31	San Jose del Golfo	El Chayal-2	SJG
11-40	La Periquera	El Chayal-2	LP
12-40	Cerro Chayal	El Chayal-2	ССН
12-40	Km 24	El Chayal-2	K24
12-40	Km 25	El Chayal-2	K25
11-12	El Pinal	El Chayal-2	EP
12-31	Aguas Caliente	El Chayal-2	AC
13-31	Barranco del Viejo	El Chayal-2	BV
13-31	Las Vacas	El Chayal-2	LV
23-04	Piedra Gorda	El Chayal-2	PG
23-14	Mogollon	El Chayal-2	МО
23-24	El Fiscal	El Chayal-2	EF
24-03-254	24-03-254	El Chayal-2	254
24-13	Azacualpilla	El Chayal-2	AZ/AZR
24-22-010	24-22-010	El Chayal-2	10
24-40	Km 19	El Chayal-2	KM
24-40	Ruta 6	El Chayal-2	RU
25-00	Chayal Chipping St.	El Chayal-2	СН
34-12	Las Vacas (Palencia)	El Chayal-2	LVP
37-12	El Pedrero 1	El Chayal-2	EP1
37-12	El Pedrero 2	El Chayal-2	EP2
37-23	Palencia	El Chayal-2	PA
75-24	Hacienda Nueva	El Chayal-2	HN
76-02	Agua Tibia	El Chayal-2	AT
13-02	San Antonio La Paz	El Chayal-3	SLP

Appendix B: Source Sampling Localities

13-21	San Antonio (N)	El Chayal-3	SAN
13-31	San Antonio (S)	El Chayal-3	SAS
13-31-237	13-31-237	El Chayal-3	237
13-32	El Remudadero	El Chayal-3	ER
13-32	El Chorro	El Chayal-3	EC
133-34	Sansare	El Chayal-3	SRE
24-41	Rio Canas	El Chayal-4	RC
50-00	Los Mixcos	El Chayal-4	LM
34-12	La Joya	El Chayal-5	LJ
2.01	San Martin J.	SMJ-1	SMJ
15.02	Pixcaya	SMJ-1	PX
15-02	Quemaya	SMJ-1	QM
15-41	El Rosario	SMJ-1	ERO
28-30	Departamental 1	SMJ-1	DP
40-24	Los Aposentos	SMJ-1	APO
40-31	San Andres Itzapa	SMJ-2	SAI
41-40	Finca Panal	SMJ-2	FP
999-99	Las Animas	IXT-1	LA
999-99	Papalhuapa	IXT-1	PH
999-99	Ojo de Agua	IXT-1	OA
999-99	Agua Blanca	IXT-2	AB
999-99	Cueva del Diablo	IXT-2	CD

Appendix C: Mahalanobis Distance Group Membership Probabilities

GROUP CLASSIFICATION USING MAHALANOBIS DISTANCE-EL CHAYAL

Results are based on the following variables:

Sr/Zr Rb/Zr Y/Zr Fe/Mn Fe Zn Ga Rb Sr Y Zr Nb Th

Best Group is based on highest membership probability > 0.001%

Membership probabilities(%) for samples in group: ONE

Probabilities calculated after removing each sample from group.

	0	NE	TV	VO	TI	łR	
ANID	Distance	Prob (%)	Distance	Prob (%)	Distance	Prob (%)	Best Group
LJT01	10.92	99.816	39.49	0.486	-542.01	0.000	ONE
LJT02	46.69	87.198	31.71	2.646	-506.47	0.000	ONE
LJT03	28.07	95.704	7.25	95.142	-84.68	0.000	ONE
LJT04	89.18	68.365	5.55	98.543	602.38	16.706	TWO
LJT05	11.18	99.798	22.29	16.968	-44.28	0.000	ONE
LJT06	36.04	92.291	20.18	24.415	-340.64	0.000	ONE
LJT07	12.90	99.642	-0.32	0.000	108.51	61.683	ONE
LJT08	11.11	99.803	16.53	42.626	-273.39	0.000	ONE
LJT09	47.54	86.785	6.67	96.618	154.94	49.609	TWO
LJT10	69.71	76.338	53.22	0.022	28.82	95.409	THR
LMZ01	3.48	99.999	4.02	99.716	224.97	38.067	ONE
LMZ02	25.01	96.830	7.66	93.929	53.20	84.025	ONE
LMZ03	18.31	98.751	17.28	38.372	-352.23	0.000	ONE
LMZ04	29.19	95.262	5.10	99.028	545.44	18.258	TWO
LMZ05	63.96	78.933	56.57	0.010	77.45	73.016	ONE
LMZ06	24.38	97.045	-4.85	0.000	372.35	25.427	ONE
LMZ08	46.89	87.103	63.22	0.002	213.73	39.555	ONE

Membership probabilities(%) for samples in group: TWO

Probabilities calculated after removing each sample from group.

	O	NE	TV	VO	TI	łR	
ANID	Distance	Prob (%)	Distance	Prob (%)	Distance	Prob (%)	Best Group
1001	-123.08	0.000	5.15	98.989	76.72	73.318	TWO
1002	129.68	38.026	21.43	19.863	111.68	60.694	THR
1003	183.50	26.585	6.11	97.715	151.99	50.244	TWO
1004	309.86	14.361	4.90	99.207	-6.85	0.000	TWO
1005	-253.22	0.000	14.33	56.553	447.26	21.737	TWO
25401	-31.85	0.000	10.07	83.457	-85.81	0.000	TWO
25402	81.77	56.419	16.26	44.362	189.25	43.220	ONE
25403	210.75	22.769	8.75	89.893	-5.46	0.000	TWO

25404	-140.31	0.000	8.22	92.005	115.33	59.589	TWO
25405	-73.39	0.000	11.47	75.245	-55.85	0.000	TWO
25406	146.01	33.826	-6.14	0.000	-49.01	0.000	ONE
25407	-57.83	0.000	4.86	99.244	-197.85	0.000	TWO
25409	-174.65	0.000	4.40	99.543	-0.50	0.000	TWO
25410	-332.83	0.000	-1.70	0.000	273.23	32.756	THR
AC07	-112.34	0.000	16.02	45.842	172.62	46.107	THR
AC08	217.89	21.916	11.69	73.902	-109.28	0.000	TWO
AC09	77.91	58.443	12.64	67.741	115.15	59.643	TWO
AC10	-183.42	0.000	14.23	57.230	192.37	42.716	TWO
AC11	-88.26	0.000	14.25	57.097	415.09	23.182	TWO
AC12	-18.32	0.000	63.45	0.002	240.46	36.188	THR
AC13	222.59	21.382	33.49	1.837	-254.78	0.000	ONE
AC14	-284.30	0.000	3.84	99.778	39.04	90.896	TWO
AC15	-251.32	0.000	7.12	95.521	279.24	32.195	TWO
AC16	-58.79	12.59	12.59	68.053	86.51	69.385	THR
AT01	-308.65	9.56	9.56	86.115	231.69	37.229	TWO
AT09	-2.07	9.46	9.46	86.594	248.59	35.273	TWO
AT10	-288.60	6.01	6.01	97.882	177.14	45.286	TWO
AT11	165.33	10.99	10.99	78.223	41.15	89.887	THR
A701	374 62	12.57	12.57	68 206	287.84	31 425	TWO
AZ05	-272 54	1.92	1.92	99 996	182 71	44 313	TWO
AZ03	-70.02	7.28	7.28	95.094	102.71	58.090	TWO
AZR01	100.65	5.10	5.10	95.094	120.40	96.164	TWO
AZR02	-100.03	0.09	0.09	90.940	40.01	80.104	1 WU
AZR03	3.72	9.98	9.98	83.900	-125.55	0.000	UNE
BV01	-210.51	10.43	10.43	81.446	258.25	34.242	TWO
CCH01	260.53	6.41	6.41	97.170	-55.88	0.000	TWO
CCH02	-39.10	8.01	8.01	92.759	3/0.80	25.170	TWO
CH05	-107.41	3.00	5.00	99.829	338.87	27.510	
CH01	219.77	52 303	4.00	0.000	8 70	0.000	
CH02	90.03	22.395	4.00	99.723	-0.19	72 242	
CH03	110.34	32.233	06.96	100.00	70.00	73.343 50.673	
CH05	-119.34	0.000	2 51	99 980	175.18	15 638	TWO
CH06	297.82	15 084	15.22	50.824	-56.87	0.000	TWO
CH07	178.40	0.000	5 73	08 313	38.35	0.000	TWO
CH08	-524.03	0.000	0.67	100.00	312 27	29.422	TWO
CH09	-280.80	0.000	3.28	99 907	71.92	75 368	TWO
CH10	-54.99	0.000	4.71	99.354	28.63	95.487	TWO
CH11	219.66	21 713	13.83	59.866	80.06	71 942	THR
CH12	-62.47	0.000	12.40	69.322	-46.32	0.000	TWO
EF01	-297.89	0.000	43.76	0.191	90.18	67.991	THR
EP01	-205.83	0.000	8.58	90.571	-59.49	0.000	TWO
EP02	-109.83	0.000	18.06	34,335	120.30	58.142	THR
EP03	-1059.51	0.000	19.16	28.976	-104.52	0.000	TWO
EP04	-424.79	0.000	27.11	6.877	191.93	42.788	THR
EP05	-178.53	0.000	43.29	0.212	1.71E3	6.272	THR
EP101	-36.33	0.000	7.16	95,415	361.10	26.090	TWO
EP102	203.26	23.724	18.82	30.559	311.87	29.452	TWO
EP103	-50.58	0.000	11.48	75.181	375.17	25.265	TWO
EP104	402.05	10.306	14.97	52,390	269.13	33,150	TWO
		10.000				22.120	

EP105	-173.32	0.000	9.77	85.066	278.83	32.233	TWO
EP106	339.63	12.798	10.57	80.690	123.19	57.329	TWO
EP107	163.88	30.022	65.49	0.001	257.56	34.314	THR
EP108	448.05	8.944	13.61	61.320	515.96	19.180	TWO
EP109	-74.46	0.000	9.19	87.924	-39.83	0.000	TWO
EP110	-132.42	0.000	13.88	59.527	285.69	31.614	TWO
EP201	429.48	9.455	17.93	34.974	-142.08	0.000	TWO
EP202	-45.25	0.000	12.06	71 526	242.90	35 908	TWO
EP203	-226.37	0.000	8 14	92 284	387.72	24 571	TWO
EI 203	204.06	15 265	11 72	72.622	110.22	0.000	TWO
EP204	294.90	13.203	11.75	1.099	-110.23	0.000	
EP205	-25.41	0.000	35.92	1.088	311.09	29.512	THR
EP206	-166.70	0.000	14.51	55.407	11.55	99.769	THK
EP208	99.34	48.363	9.44	86.695	184.92	43.937	IWO
EP209	230.98	20.481	40.22	0.422	1.3/E3	7.801	ONE
EP210	-24.16	0.000	21.85	18.465	130.61	55.333	THR
HN01	-109.61	0.000	9.32	87.264	87.39	69.045	TWO
K2401	-403.09	0.000	17.25	38.673	439.28	22.078	TWO
K2501	-72.61	0.000	1.56	99.999	398.90	23.985	TWO
KM01	-17.63	0.000	9.82	84.803	168.47	46.886	TWO
KM02	140.29	35.210	4.05	99.707	210.56	39.995	TWO
KM03	158.07	31.180	15.81	47.092	408.73	23.491	TWO
KM04	1.62	100.00	18.84	30.453	49.72	85.722	ONE
LP01	111.54	43.739	67.12	0.001	33.97	93.232	THR
LP02	-145.27	0.000	24.62	11.149	404.32	23.710	THR
LP03	234.66	20.106	18.21	33.548	162.23	48.105	THR
LP04	-239.97	0.000	1.50E3	0.000	176.62	45.380	THR
LP05	-307.09	0.000	6.85	96.218	466.47	20.956	TWO
LV01	168.60	29.131	-8.96	0.000	34.57	92.963	THR
LV02	552.00	6.768	21.29	20.361	22.33	97.695	THK
	-191.45	0.000	8.31	91.657	161.88	48.177	TWO
LV04	-149.94	0.000	13.39	02.821	-04.31	0.000	TWO
	-339.77	0.000	5.30	98.005	119.31	38.425	TWO
LVP02	328.04	15.540	3.44	98.081	180.44	44.704	TWO
	-21.42	21.440	27.80	08 507	-70.27	0.000	
LVP04	221.33	21.449	J.J0 13.11	98.307	12.90	99.041 63.248	
LVP05	355.69	12.068	17.24	38 603	313.00	29 290	TWO
MO01	199.68	24 203	9.96	84.027	-106.89	0.000	TWO
M001	-17/ 29	0.000	14.12	57.987	424.55	22 738	TWO
M002 M003	-601.63	0.000	19.75	26 322	745.49	13 763	TWO
PA01	44.00	80 599	5 88	98 094	266.06	33 451	TWO
PA02	-17 34	0.000	3.93	99 750	51 58	84 814	TWO
PA03	-66 52	0.000	7 73	93 715	119 69	58 315	TWO
PA04	-198.72	0.000	9.56	86.089	281.45	31,993	TWO
PG01	-231.35	0.000	5.76	98.261	225.43	38.008	TWO
PG02	-201.94	0.000	14.06	58.352	53.45	83.905	THR
PG03	312.83	14.191	16.26	44.363	365.96	25.799	TWO
PG04	132.51	37.241	10.77	79.522	365.01	25.856	TWO
PG05	112.69	43.337	12.24	70.343	537.00	18.513	TWO
RU01	58.82	69.986	496.84	0.000	156.28	49.326	ONE
RU02	38.43	94.791	13.88	59.532	-184.09	0.000	ONE
RU03	4.92	99.992	15.70	47.785	-163.20	0.000	ONE

RU04	-60.23	0.000	25.12	10.127	704.54	14.494	THR
SJG03	123.75	39.758	9.71	85.372	8.03	99.953	THR

Membership probabilities(%) for samples in group: THR

Probabilities calculated after removing each sample from group.

	0	NE	TV	VO	TI	HR	
ANID	Distance	Prob (%)	Distance	Prob (%)	Distance	Prob (%)	Best Group
23701	1.22E3	2.228	312.34	0.000	20.12	99.387	THR
23702	307.34	14.507	38.39	0.621	53.97	93.082	THR
23704	334.76	13.034	75.11	0.000	50.14	93.954	THR
23705	322.36	13.668	99.69	0.000	20.97	99.301	THR
EC01	1.80E3	1.280	60.84	0.004	6.95	99.992	THR
EC02	1.49E3	1.673	148.85	0.000	31.37	97.825	THR
EC03	1.07E3	2.701	116.89	0.000	14.15	99.821	THR
ER02	1.12E3	2.522	42.31	0.259	28.98	98.226	THR
SAN01	1.08E3	2.659	93.83	0.000	55.04	92.836	THR
SAN03	1.31E3	2.019	145.34	0.000	85.29	86.025	THR
SAN04	987.64	3.022	66.53	0.001	12.66	99.884	THR
SAS04	776.39	4.237	138.69	0.000	55.46	92.740	THR
SAS07	317.96	13.905	148.13	0.000	33.37	97.468	THR
SAS10	916.53	3.358	127.07	0.000	37.53	96.669	THR
SLP01	417.58	9.810	60.24	0.004	56.67	92.463	THR
SRE01	167.48	29.340	66.92	0.001	976.97	34.924	THR

GROUP CLASSIFICATION USING MAHALANOBIS DISTANCE-SAN MARTIN J.

Results are based on the following variables:

Sr/Zr Rb/Zr Y/Zr Fe/Mn Mn Fe Zn Ga Rb Sr Y Zr Nb Th

Best Group is based on highest membership probability > 0.001%

		JIL1		
ANID	Distance	Prob (%)	Best Group	
APO06	39.24	24.118	JIL1	
APO07	6.82	99.308	JIL1	
APO09	7.82	98.719	JIL1	
APO10	8.64	98.035	JIL1	
DP01	19.37	73.072	JIL1	
ERO01	9.09	97.583	JIL1	
PX01	41.28	21.285	JIL1	
PX02	14.48	87.458	JIL1	
PX03	69.25	4.058	JIL1	
PX04	24.69	56.491	JIL1	
PX05	26.44	51.406	JIL1	
PX06	23.26	60.815	JIL1	
PX07	16.61	81.548	JIL1	
PX08	17.59	78.596	JIL1	
PX09	3.66	99.972	JIL1	
PX10	9.15	97.520	JIL1	
QM01	-9.66	0.000		
QM02	14.98	86.143	JIL1	
QM03	4.72	99.888	JIL1	
QM04	8.97	97.715	JIL1	
QM05	30.27	41.378	JIL1	
QM06	5.61	99.729	JIL1	
QM07	13.06	90.906	JIL1	
QM08	39.58	23.617	JIL1	
QM09	12.87	91.324	JIL1	
QM10	15.47	84.814	JIL1	
SMJ06	23.46	60.214	JIL1	
SMJ07	45.58	16.345	JIL1	
SMJ08	10.45	95.825	JIL1	
SMJ09	33.16	34.898	JIL1	

Membership probabilities(%) for samples in group: JIL1

Probabilities calculated after removing each sample from group.

GROUP CLASSIFICATION USING MAHALANOBIS DISTANCE-IXTEPEQUE

Results are based on the following variables:

Sr/Zr Rb/Zr Y/Zr Fe/Mn Mn Fe Zn Ga Rb Sr Y Zr Nb Th

Best Group is based on highest membership probability > 0.001%

Membership probabilities(%) for samples in group: IXT1

Probabilities calculated after removing each sample from group.

	IXT1		
ANID	Distance	Prob (%)	Best Group
LA01	86.03	69.570	IXT1
LA02	14.05	99.504	IXT1
LA03	-2.65	0.000	
LA04	17.87	98.848	IXT1
LA05	-9.41	0.000	
LA06	89.30	68.321	IXT1
LA07	58.53	81.472	IXT1
LA08	40.18	90.355	IXT1
LA09	45.28	87.889	IXT1
LA10	14.23	99.480	IXT1
LA11	-17.52	0.000	
LA12	130.24	55.430	IXT1
OA01	-734.94	0.000	
PH01	91.98	67.324	IXT1
PH02	6.77	99.979	IXT1
PH03	16.02	99.204	IXT1
PH04	7.67	99.962	IXT1

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