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Exploring Potential Applications of Portable X-ray Fluorescence on Earthen Materials from Southeast Mesoamerica

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Exploring Potential Applications of Portable X-ray Fluorescence on Earthen Materials from Southeast Mesoamerica

by

David Rafael McCormick

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Arts Department of Anthropology College of Arts and Sciences University of South Florida

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Abstract

The use of geochemical analysis for characterization studies of archaeological material has been increasing for decades. In recent years, advancements in X-ray fluorescence (XRF) instrumentation have led to hand-held portable XRF (pXRF) instruments capable of on-site, rapid, non-destructive analysis. The addition of pXRF to the archaeologist’s toolkit has the potential to revolutionize geochemical characterization studies as research design can be informed by field analysis, once off-limits museum collections may now be analyzable, and data can be gathered on in-situ objects without disturbing their context. This new instrumentation has shown promise in characterization studies on a variety of archaeological materials, including ceramics. Particularly, it has been shown to generate data useful in distinguishing the geochemical provenance of artifacts. While most existing provenance studies that employ pXRF involve obsidian, it is possible that pXRF is a suitable analytical tool for ceramics as well, since instrumental neutron activation analysis (INAA) and laboratory XRF have both been used in provenance studies of obsidian and ceramics. This thesis reports research that utilized a Bruker hand held pXRF analyzer to study ceramics and plaster floors from Classic Period (ca. AD 250-1000) archaeological sites in southeast Mesoamerica. The data gathered from this analysis are used to examine the ability of pXRF to address archaeological questions of archaeological provenance on ceramic material and human activity patterns on archaeological plaster. The data gathered on ceramic material is analyzed to determine if “valley profiles” (or “chemical fingerprints”) can be created for samples excavated in the
same valley and to investigate inter-valley trade. Data from the plaster samples is examined to determine if pXRF can detect human activity patterns on plaster floors and, if so, if the activity is identifiable. The results suggest that, while pXRF results can be used to create “valley profiles” for provenance research, it is difficult to ascertain if it can be used to identify items of trade. This investigation also shows that, while pXRF data can identify human activity on plaster, it is difficult to determine what those activities were. This leads to the conclusion that pXRF has potential for both provenance and prospection studies on earthen materials. However, methodological development is necessary to fine tune research design. This thesis contributes to a greater understanding of the potentials and limitations of pXRF instrumentation in characterization studies of archaeological materials as well as understanding cultural-historical details in Classic southeast Mesoamerica.
Chapter 1: Introduction

In this thesis, I examine the results of geochemical analyses on geoarchaeological materials from the Classic Period (ca. AD 250-1000) in southeast Mesoamerica with the aim of assessing the efficacy of using portable X-ray fluorescence spectrometry (pXRF) in compositional studies of earthen materials from the region. A number of chemical studies have been conducted on a wide range of materials from this area that date to the Classic Period (e.g., Aoyama 1994; Sheets et al. 1990 for obsidian; Luke and Tykot 2002, 2007; Luke et al. 2006 for marble; Bishop et al. 1986; Neff et al. 1999; Reents-Budet et al. 2004 for ceramics; Canuto et al. 2010; Rothenberg 2010; Wells 2004; Wells et al. 2007 for soils; and Goodall et al. 2006; McVey 1998 for plaster). The application of geochemical analyses to determine a specimen’s provenance examines the chemical composition of the material so as to ascertain the material’s place of origin. Geochemical analyses have also been applied to archaeological prospection. This term is applied to the use of various techniques to prospect for archaeological features, including sites and human activity patterns.

Handheld pXRF instruments are relatively new to archaeologist’s analytical toolkits, and there has been a heated debate as to its efficacy in addressing archaeological questions (Shackley 2010). While some vendors purport the ability of their pXRF to be used for a wide variety of archaeological investigations, many archaeologists question pXRF’s ability to produce reliable and valid results, and caution against its misuse (Shackley 2010). Here, I discuss the results of experimental investigations designed to
test the ability of Bruker Tracer III-V and III-SD pXRF instruments to produce reliable and accurate data to answer questions about provenance and prospection. Portable XRF has the potential to change archaeological analysis, because of its portability and non-destructive nature. Portability enables analysis to be done on-site (be it in a lab, museum, or field site) ameliorating the need for off-site analysis in often distant specialized laboratories. Non-destructive analysis has become increasingly important since the mid-twentith century due to the responsibility of archaeology as a discipline to stakeholders, including many descendant groups who regard the destruction of cultural heritage as unacceptable (Joyce 2011).

X-ray fluorescence spectrometry has long been used for compositional studies of archaeological material (Shackley 2010, 2011; e.g., Hughes 1983, 1984; Jack 1971, 1976; Jack and Carmichael 1969; Jack and Heizer 1968; Jackson 1974, 1986; Stross et al. 1983). Recent innovations in XRF technology have generated a variety of desktop, portable, and handheld XRF instruments that have been used in studies asking an array of questions about the past. Portable XRF instruments allow for rapid, non-destructive, high-resolution, multi-elemental analysis in both laboratory and field settings. In this thesis, I investigate two related research questions, both of which concern the applicability of pXRF in compositional studies in southeast Mesoamerica. First, I investigate the use of pXRF for determining the provenance of archaeological ceramics. Second, I investigate the use of this instrumental technique in the prospection of archaeological features (i.e., human activity patterns) on plaster surfaces.

My goal with regard to the first research question is: What is the applicability of pXRF in provenance studies of clays and ceramics from the neighboring regions of the
Naco (Honduras) and Motagua (Guatemala) valleys? Ceramics have long been a material class investigated by archaeologists for understanding human society. Differentiating local and non-local wares is an important method of investigating internal site dynamics and interregional interaction. Often, hypotheses are made about power dynamics and the interactions between polities based on visual analysis of ceramic assemblages. Geochemical analyses can test these hypotheses to examine whether certain pottery types depicting a non-local style are, in fact, imports rather than local imitations. Collection of elemental data on ceramic collections allows statistical scrutinization of these ceramic assemblages. The geochemical method most commonly used for the collection of elemental data on archaeological material in Mesoamerica is instrumental neutron activation analysis (INAA). INAA has been used to identify local reference groups that can be used to chemically distinguish imports. Data gathered with laboratory XRF and pXRF have been compared to reference groups created with INAA data on obsidian in the Maya Lowlands (Nazaroff et al. 2010). To date, no such study exists for pXRF on ceramics from this region. As this thesis documents, I found that pXRF data can be used to generate ceramic profiles that distinguish sherds to their valley of origin.

With regard to my second research question, I explore pXRF’s applicability in archaeological prospection on plaster floors from the site of El Coyote, Honduras. The surfaces on which human activities took place in antiquity are of particular interest to archaeologists, because they have been shown to capture and preserve traces of these activities. Investigations into soil chemistry in the Maya region have proven fruitful in investigating the functions of plazas and other open spaces (e.g., Canuto et al. 2010; Rothenberg 2010; Wells 2003) as well as household areas (Terry et al. 2004; Wells et al.
Plaster floors have been demonstrated to trap and preserve a variety of chemical compounds indicative of past human activity over very long periods at various sites in the Mesoamerica (e.g., Barba 1996, 2000, 2007; Barba and Augustín 1992; Hutson and Terry 2006; Pecci et al. 2010; Terry et al. 2004). Here, I study the use of pXRF’s ability to answer questions about human activity patterns in ancient times and compare results of soil analysis with ICP-MS and pXRF conducted on plaster floors from the same provenience. My findings indicate that pXRF can be used to identify human activity areas but that defining those activities may be difficult.

Organization of Thesis. I have organized this thesis into six chapters. In Chapter 2, I provide an overview of the study area, southeast Mesoamerica. This chapter is divided into four sections, the first three of which are concerned with regions of southeast Mesoamerica where material analyzed in this thesis were excavated. The local geography, the valleys’ geology and geomorphology, and cultural history are discussed here. I conclude the chapter with a brief discussion of neighboring regions of southeast Mesoamerica. In Chapter 3, I discuss previous geochemical analyses performed on southeast Mesoamerican materials involving questions of archaeological provenance and prospection. This chapter ends with a discussion of pXRF, its instrumentation, how it has been used in provenance and prospection studies, and addresses the instrument’s strengths and weaknesses. In Chapter 4, I discuss my analyses and their results. The research design, analytical process, and statistical procedures are outlined here. Additionally, this chapter includes my quantitative discriminant function analysis on ceramic compositional data to ascertain its efficacy in creating ceramic profiles and examination of the plaster data to determine applicability in answering questions about
human activity patterns. I discuss the results of these analyses in Chapter 5, returning to the archaeological questions this study was designed to address. Here, the level of applicability of data gathered with pXRF in answering the original questions is examined. In the final chapter, I discuss the implications of this research in the larger corpus of geochemical studies on southeast Mesoamerican archaeological materials, the applicability of pXRF in this region and its ability to answer archaeological questions. Relevant points from the previous chapters are revisited as well as concluding commentary.
Chapter 2:
The Archaeological Setting: Southeast Mesoamerica

In order to explain the significance—both behavioral and natural—of the chemical variation in the earthen materials examined in this thesis, it is important to understand the geology, geomorphology, and cultural history of the region from which these materials are derived (Neff et al. 1994; Vaughn and Neff 2002). While the manufacturing process of a product is subject to innovation and change, that product is ultimately limited by the materials available (Neff 1993). In this chapter, I discuss the environment and archaeology of the three regions (valley systems) from which my samples derive.

Southeast Mesoamerica is delineated differently by different scholars, but generally encompasses part of northeastern Guatemala, western Honduras, and much of El Salvador (Longyear 1947; Lothrop 1939; Thompson 1970; Schortman 1986; Sheets 2000). It is loosely defined by the “the distribution of certain material items whose conjunction reflects a unitary phenomenon known as ‘Maya Culture’ (Schortman 1986:114, 116-117; Sharer 1988). This area is often depicted as a transitional region between Maya and non-Maya languages and cultural traditions (Henderson 1977; Henderson et al. 1979). The southeast zone contains both Maya and non-Maya polities, the latter of which show differential participation in Maya culture as expressed through the material record (Schortman 1993; Schortman and Urban 1986; Sharer 1988). For the purpose of this discussion, the boundaries demarcated by Schortman and Urban (1988) are used. This area includes the two Classic Maya centers of Copán and Quiriguá defined
by Webster (1988) and Sharer (1988) as part of the “Southeast Lowland Maya Zone” and the “Greater Southeast Zone,” which surround both centers (Figure 2.1). Schortman and Urban (1988) divide the southeast into five zones: Lower Motagua, Naco, Sula Plain, Lake Yojoa-Comayagua, and Highland. While the nomenclature of these zones has slightly changed, I adhere to their geographic boundaries. The Classic Maya Centers of Copán and Quiriguá are located in the Highland Zone and Lower Motagua Zone respectively, and are located at the western edges of the southeast region. The material that was analyzed in this thesis comes from archaeological contexts in the Lower Motagua and Naco zones, which are noted to have participated in an interaction network referred to as the Lower Motagua-Naco Valley network (McFarlane 2005). Sites in this interaction network, except for Quiriguá, a Classic Maya Center, are non-Mayan and show differential adoption of Maya material forms (Schortman 1986). Classic populations of these valleys certainly lived in ranked societies; however, the level of stratification varied considerably.

The region itself varies topographically and environmentally with highland zones in eastern Guatemala, El Salvador and parts of Honduras, to rolling hills of western Honduras and the lowland plains of Honduras's Caribbean coast. It is clear from past archaeological investigations that the inhabitants of this region interacted extensively with each other and in doing so had interactions that extend far to the north and west into Mesoamerica as well as south and east into Central America (e.g., see Adams 2005; Hirth 1988; Joyce 1985; Luke and Tykot 2008; Urban and Schortman 1986).
Archaeological interest in the southeast began in 1839 when John Lloyd Stephens arrived at the site of Copán in modern day Honduras. Two years later Stephens (1841) published *Incidents of Travel in Central America, Chiapas and Yucatán*, and both the sites of Copán and Quiriguá received public attention.

The earliest investigations in the region concentrated on the monumental centers of Copán and Quiriguá (e.g., Gordon 1896; Hewett 1911-1913, 1916; Longyear 1952, Maudsley 1889-1902; Morley 1913, 1914, 1920, 1935) and until the 1960s the area received only restricted attention (but see Canby 1949, 1951; Berlin 1952; Boggs 1944, 1950; Gordon 1898; Longyear 1944, 1947; Popenoe 1934, 1935; Sapper 1895 Stone
1941; 1957; Stromsvik 1936; Strong et al. 1938; Yde 1938). Beginning with the Los Naranjos project around Lake Yojoa, Honduras during the late 1960s and the Chalchuapa project in eastern El Salvador (1966, 1969-70) a more systematic and comprehensive approach was taken to developing a picture of how the Maya and non-Maya of the southeast interacted. The aforementioned studies were followed by extensive studies throughout the region including large-scale investigation of Quiriguá and Copán, which included the hinterlands of these sites. Of particular interest to this study are the Quiriguá Archaeological Project (QAP; 1974-1979), the Naco Valley Project (NVP; 1976-1996) and the Cacaulapa Valley Project (CVP; 1999-present) from which the materials for this research came.

**Naco Valley**

Named after the modern town located at its center, the Naco Valley (NV) encompasses 96 km$^2$ of generally flat and fertile land between the Lower Motagua Valley (LMV) and the Sula Plain in northwest Honduras (Figure 2.2) (Schortman and Urban 1994; 1996; Schortman et al. 2001; Urban 1986a, 1986b; Urban and Schortman 1988). The Sierra de Omoa Mountains on the north and west and low hills on the east and south circumscribe it. The valley ranges approximately 100-200 m above sea level with about 1300 mm of precipitation annually (Schortman and Urban 1994; Schortman et al. 2001; Urban 1986a, 1986b). Three rivers provide a year round source of water the Manachaguala, Naco and Chamelecón, which are fed by four large streams and an extensive network of seasonal quebradas (Urban 1986a, 1986b). The Sierra de Omoa Mountains are composed of metamorphic rock, particularly gneiss and schist, from the Paleozoic age (West
1964:67). The lower hills of the east and south contain limestone, notably three of these Loma de Jicaro (southwest), Jutipa Hill (south-central) and Cerro Miravalles (east) are primarily limestone. The southern hills contain shells, have inclusions of chert and some poor quality marble, while the eastern limestone lacks these attributes (Urban 1986a). The geomorphology of the Naco Valley produces a complex soil picture (Urban 1986a:16). The metamorphic rocks of the Sierra de Omoa generally contribute to poor soil conditions and the limestone of the hills cultivating favorable soils (Stevens 1964:268). Urban (1986a:17-20) divides the soils of the valley into four zones: 1- red; 2- tan; 3- black-brown; 4- black (Urban 1986a:676). The red zone follows the base of the western hills stretching east with decreasing intensity into the tan soil zone. The loamy soils of the red zone are shallow, dry and reportedly infertile. The tan soil zone is a more matured derivative of the red soil zone. The soils are silty to clayey, and can reach depths of > 2 m near the banks of the Chamelecón. The silty to clayey soils of the black-brown (to brown) zone are found in the hills north of the Rio Manchaguala, may reach depths of > 2 m. Although these soils and the red zone soils both have metamorphic parent rock, the abundance of deciduous and semi-deciduous trees have enriched this brown soil making it ideal for planting. The black earth zone is located east of the Chamelecón and is clayey in texture. A small band of thin tan soil is found on the east side of the Chamelecón. The vast majority of the soils in the valley are colluvial. Alluvial soils are restricted to a tightly circumscribed zone around the valley's waterways.
Figure 2.2 Map of Naco Valley, Honduras, settlement distribution during Period 5-B (AD 775-950). Reproduced from Urban 1986b:Figure 3.

Environmentally the valley is situated between the hot, humid, heavily vegetated Sula Plain and the cooler, elevation forests of the Western Honduran Highlands (Henderson 1977; Henderson et al. 1979; Rothenberg 2010; Urban 1986a). The
Chamelecón has its headwaters near the site of Copán in the Highland Zone to the southwest. In the Naco Valley the Chamelecón widens its breadth providing a large, level and fertile floodplain (Henderson 1977, Henderson et al. 1979), before reaching the Sula Plain and eventually draining into the Caribbean Sea. Most prehispanic settlements in the Naco Valley are located on the flat terraces of the valley near water, and many have been washed away since abandonment (Henderson et al. 1979; Urban 1986a). According to Escoto (1964) the Naco Valley is on the border of two similar climatic zones in the tropical lowlands of southeast Mesoamerica. Generally speaking the valley experiences a dry season beginning in January to May and a rainy season peaking in September, there is also a short dry period usually in early July to mid-August known as a canícula (Perez personal communication 2012). Humidity remains high all year averaging 80 percent with its peak at the end of the dry season. Temperature is fairly stable with highs between 30-35°C and lows 20-25°C.

**Cultural History.** Archaeological investigations have shown a pre-Colombian occupation sequence beginning in the Middle Preclassic (ca. 1050-400 BC) until the Spanish conquest in the sixteenth century. The earliest settlements are represented by pattern-burnished tecomates (neckless jars) and vertical and flaring-walled bowls, plates and cylinders found at 23 sites across the valley (Urban 1986a; Urban et al. 2002:136; Wells 2003). Earthen platforms at minimally three of these sites suggest a two-tiered hierarchy during this period. Each site seems to have developed into an administrative hub during the Late Preclassic (ca. 300 BC – 300 AD, here), but the degree of autonomy of each site is unknown. By the end of this period Santo Domingo seems to have emerged as the valley capitol (Schortman and Urban 2004:321). What is clear is that during the
Preclassic the people of the Naco Valley were engaged in interregional interactions with other areas of Southeast Mesoamerica. The ceramic record shows stylistic similarities to neighboring valleys and as far flung as the Late Preclassic polity of Chalchuapa in modern day El Salvador (Urban et al. 2002).

In the Early Classic (ca. 300-600 AD) settlement moved toward the center of the valley, while La Sierra and two other large sites (113 and 116) were founded at that time. Interregional interaction is evidenced by the presence of imported polychromes from the Ulúa polychromes and stylistic affinity of red-decorated pottery types (Magdalena in the Naco Valley) and those found in neighboring Valleys (La Isla in Ulúa and Prospero at Copán).

Much like other zones in the southeast, the Late Classic (ca. 600-900 AD) was a period of population growth, during which La Sierra clearly becomes the seat of power in the Naco Valley. Over fifteen sites contain monumental architecture and may represent administrative complexes and/or elite residences. All Late Classic sites follow the same architectural scheme: structures are irregularly arranged around an open plaza without orthogonal orientation (Urban and Schortman 1988:229). It is clear that the ruling elite of La Sierra were able to consolidate power and control labor as evidenced by the (minimally) 468 structures that make up the site. At ten times the size of any valley contemporaries La Sierra was a hub of trade and manufacture. Imported obsidian was processed and redistributed throughout the valley in the form of prismatic blades, as were ceramic censers, pottery and figurines made from local clay (Douglass 2002; Ross 1997; Schortman and Urban 1994). A marine shell workshop at La Sierra has revealed 1,256 fragments along with distinctive chert tools showing use wear consistent with engraving
and/or cutting (see Schortman and Urban 1996). The paucity of finished shell artifacts and singular shell workshop suggest that worked marine shell was an important elite controlled export, possibly to the Copán area (Schortman and Urban 1996:106). Worked shell may well have been La Sierra’s main currency in acquiring the imported goods the ruling elite required. Interregional exchange with specific valleys can be inferred by the non-local ceramic types found in the Naco Valley which include, Tipon types from the Lower Motagua Valley (Schortman 1993), Copador (presumably) from Copán, and Ulúa Polychromes from the lower Ulúa region (Joyce 1993). It is important to note that Naco, unlike the neighboring Sula Plain is lacking in Red-painted Usulután vessels and while Copador and Ulúa polychromes are found, they are rare and all of the fine wares mentioned above are restricted to La Sierra.

Populations in the valley plunged from the Terminal Classic to the Early Postclassic (ca. 950-1250 AD). Of the 16 sites recorded for this period, most are found on high ground in the northwest part of the valley, built of materials possibly pilfered from La Sierra (Wells 2003:61-62).

To recap, the Naco Valley saw a steady increase in population size and nucleation during the Middle Preclassic. In the Early Classic two (minimally) administrative centers, including La Sierra emerged in possible competition with each other. La Sierra emerged as the valley capital during the Late Classic. The ruling elite consolidated their power through monopolization of imported obsidian and foreign style polychromes, in conjunction with the local production of ceramic censers, pottery, figurines, and obsidian tools. Additionally the export of worked shell may have contributed to the valley elite’s
ability to assert power through external, elite ties. The Late Classic population decline is likely tied to the same fate as many other sites in the southeast Mesoamerica.

**Lower Motagua Valley**

The Lower Motagua Valley is located in the northeastern corner of southeast Mesoamerica. At the southwestern edge of the valley is the Classic Maya Center of Quiriguá, a site on the eastern border of the Classic Maya Lowlands. The Lower Motagua Valley encompasses 1800 km² of tropical lowlands in the Department of Izabal, Guatemala. Circumscribed by the Sierra de Las Minas and Espíritu Santo mountains on the northwest and southeast respectively, this valley of rich agricultural land, stretches from Quiriguá at its southwestern corner to the Caribbean coast at the Motagua’s terminus. The Lower Motagua River is fed by ten major tributaries, which provide the valley with a perennial source of water (Schortman 1993; Wells 2003), and to the southeast, passes over the high mountains into adjoining regions in Honduras (Schortman and Nakamura 1991; Wells 2003).

The Lower Motagua Valley is physiographically located in the province of “Old Antillia” an area of rugged mountain ranges encompassing northern Central America and the islands of the Greater Antilles (Schortman 1984; West and Augelli 1976:Figure 2.1). Escarpments in the valley contain metamorphic (schist, gneiss, marble and granites), igneous (rhyolites) and sedimentary (sandstone) rock, and a few restricted gold deposits (Schortman, 1984). The valley floor is covered with alluvial soils deposited regularly by the Motagua River and its tributaries. Situated in an area of “general earthquake activity” (West and Augelli 1976:Figure 2.1), the valley lies on the Motagua fault whose last major
activity caused extensive damage within the Lower Motagua and Guatemala (see Bevan and Sharer 1983; Schortman 1984; 1993).

Broadly speaking, the soils of the Lower Motagua Valley are distinguishable into three types (Schortman 1984, 1993). First, the broad floodplain is covered with thick deposits of azonal alluvial soils discharged periodically by the Motagua and its tributaries (Stevens 1964:Figure 7), providing “prime agricultural land” (Schortman 1984, 1993; West and Augelli 1976:48). The second soil type is found on the floodplain in areas of poor drainage that can become waterlogged (West and Augelli 1976) causing the soils to be heavily leached and acidic (Schortman 1984; 1993; Stevens 1964:Figure 7) making them of limited use to the valley’s ancient inhabitants. Many of the sites surveyed in the Quiriguá Archaeological Project (QAP) (Choco, Las Quebradas, Playitas, Quebrada Grande and Comanche Farm) had waterlogged soils and areas of standing water, but whether this condition also pertained to the site prior to abandonment is unknown (Schortman 1984). The Espiritu Santo hills on the southern end of the valley have zonal red and yellow podzolic-lateric soils (Stevens 1964:Figure 7). To the north the Sierra de las Minas’ soils are zonal reddish brown and yellowish brown lateric (Stevens 1964:Figure 7). The northern valley border soils also contain brown calcareous lithosols. This second group of soil is considered less fertile than those of the valley floor (Schortman 1984, 1993). The soils of the Lower Motagua Valley consist of high, well drained and highly productive flood plain land (1), less productive land in poorly drained swampy flood plain land (2) and the soils of the surrounding hills (3) (Schortman 1984, 1993).
The Lower Motagua Valley is located in the Tropical Rainforest Zone (Escoto 1964) and experiences both high temperatures and rainfalls throughout the year with a reduction in rainfall from January to April (Escoto 1964; West and Augelli 1976:45; Schortman 1993). The Rio Motagua’s headwaters begin in the Highlands of Guatemala and continue for approximately 350km where it meets the Caribbean Sea. The valley is located in ‘Tierra Caliente’ zone of Middle America with daily highs between 29-30°C and lows between 21-24°C (West and Augelli 1976). Easterly trade winds bring moisture-rich air from the Caribbean resulting in an average of 2000 mm annual rainfall, with no defined dry season (Ashmore 2007; Schortman 1993; West and Augelli 1976). The combination of temperature and precipitation are ample to support two annual harvests (Ashmore 2007:17).

**Cultural History.** The earliest evidence of occupation in the Lower Motagua Valley comes from sporadic ceramic assemblages at riverine sites dating to the Late Preclassic, 300 BC – AD 200, suggesting the Motagua’s early significance as a channel of commerce and communication (Sharer 1988:36; Schortman 1993; Wells 2003). The evidence of this early occupation in the artifact record (ceramics and lithic) is sparse, and much of it comes from disturbed contexts (Ashmore 1984, 2007; Sharer 1988).

All evidence of occupation deviates from Preclassic Maya Highland tradition (see Demarest and Sharer 1986), suggesting the valley’s early inhabitants were non-Maya. Beginning in the Early Classic, AD 300-600, occupation centers at the civic-ceremonial center of Quiriguá, a site that displays all the hallmarks of a Classic Maya Center (see Sharer 1986; Schortman 1984, 1993). The earliest surviving buildings of what became

Quiriguá were built during Ashmore’s (1984; 2007) Periphery Time Span (PTS) 5, and Sharer’s (1978) Acropolis Time Span (ATS) 4, ca. AD 400-600. The initial building campaign begat two small sites (Ashmore 2007; Sharer 1978). The first of these building
agglomerations contains Monument 26, a stela which bears the Long Count Date of 9.2.18.0.0(?) (ca. AD 493) (Ashmore 1984; Jones and Sharer 1980; Sharer 1990:70). The second stela (Monument 21) carries a dedicatory Long Count date of 9.2.3.8.0 (ca AD 478) and is located at a site north of the flood plain.

A flood event indicated in the stratigraphic record damaged the site and covering it in silt and interrupts the occupation sequence until about AD 650 (Sharer 1988:39). In the following Late to Terminal Classic Period (AD 650-900) Quiriguá and the rest of the Lower Motagua Valley experienced a pronounced increase in both population size and density. Building at Quiriguá resumes with renewed vigor and numerous Lower Motagua Valley sites are founded and flourish as well. It is suggested that the Late Classic population of Quiriguá is the result of elite immigration from the Petén, Tikal in particular (Sharer 1988). Quiriguá’s city plan is reoriented, possibly as a reaction to a new course for the Motagua (Sharer 1988:39). Early on Quiriguá’s site core is expanded, the acropolis, representing the elite administrative center and residences is restored and enlarged, cut stone masonry pyramids and a ball court are built. Some scholars (e.g., Sharer 1988) have proposed that the building campaign in the early Late Classic was sponsored by elites from Copán marks the beginning or solidifying of a vassal-lord relationship between Quiriguá and Copán, in which Copán was dominant. Quiriguá was geographically positioned to take advantage of both the Motagua’s fertile flood plain and interregional trade routes both east-west along the river and north-south across the valley (Sharer 1988). The combined advantages of the site allowed Quiriguá to grow exportable crops like cacao and granted easy access to imported raw materials such as obsidian and jade. The site’s core was expanded throughout this period with a punctuated fluorescence
of building and the erection of stelae by K’ak’ Tiwil Chan Yopaat, Quiriguá’s most illustrious king. According to Monument 5, on the Long Count date of 9.15.614.6 (May 3, AD 738) the Quiriguá ruler captured and beheaded Copán’s 13th ruler, Waxakalajun Ub’ ah K’awil (“18 are the Images of K’awil”) (see Fash 2001:129; Marcus1976; Sharer 1978:67).

As mentioned above the wider valley also experienced a boom in population size and density in the Late Classic. The population was aggregated into many valley centers of varying sizes and functions. Sharer breaks down the settlement hierarchy (see 1988:56-58; Schortman 1984, 1993) into three groups: Primary, Intermediate and Secondary. All four of the Primary sites (Las Quebradas, Playitas, Quebrada Grande, and Choco) are found along the southeast side of the valley strategically positioned to influence the movement of goods across the Espiritu Santo Mountains. Architecturally the wider valley is distinctly LMV, which is to say unlike Quiriguá its sites display a non-Maya settlement pattern. Each of the Primary and Intermediate centers contains the valley’s dominant architectural focal group, the quadrangle, a residential and administrative complex for elites (Sharer 1988; Schortman 1986, 1993). The frequency of buildings attenuates with distance from the quadrangle groups. The smaller structure aggregates represent a non-elite population subservient to their quadrangle dwelling counterparts (see Urban and Schortman 1986). Almost exclusively monumental architecture in the wider valley is made of unfaced river cobbles enclosing packed earth fills. Only one structure (Playitas Str. 200-77) has plastering and architectural decoration (Schortman 1984, 1993; Berlin 1952). The few monuments (8) found in the wider valley are found within large courts, not in open plazas as at Quiriguá (and other Classic Maya
sites). Evidenced by the high frequency of *incensario* sherds in these courts, it is likely these spaces served as hubs of private, elite ritual activity.

The wider valley sites are seen to represent independent power centers, each holding influence over a restricted segment of valley resources and a specific avenue of communication (Sharer 1988:57). However, while independent, these centers were economically (and to some extent politically) dependent on Quiriguá, as evidenced by their pronounced, yet brief development. Each site was ostensibly founded, enlarged and abandoned concurrently with Quiriguá’s Late Classic florescence (Sharer 1988). It does not appear that any one elite group at these sites enjoyed the same level of power as at Quiriguá, instead the dispersed arrangement of elite groups suggests the independence of ranked elite factions (Urban & Schortman 1988), particularly at Las Quebradas and Playitas.

The death of K’ak’ Tiliw Chan Yopaat, in AD 784 marks a decline in the quantity and quality of monumental building at Quiriguá. It also marks a shift in ceramic inventory, reflecting trade contacts and possibly the arrival of coastal Maya populations. Whatever the case was the valley depopulates quickly after about AD 810. Sometime after AD 900 Quiriguá is abandoned, along with most of the Lower Motagua Valley centers (Sharer 1988:42). Evidence of continued occupation continues into the Postclassic, probably in agricultural villages in the Lower Motagua Valley as deduced by reports of Postclassic ceramic types and other temporal markers (see Schortman 1993).

In Summary, Pre-Columbian occupation in the Lower Motagua Valley began in the Late Preclassic as evidenced by scattered assemblages along the Motagua’s banks. In the Early Classic a dynasty was founded (possibly with an immigration of an elite
population from the Petén) at Quiriguá. The developmental trajectory of Quiriguá was severely disrupted by a flood event halting construction until a renaissance in the early Late Classic, possibly under the auspices of Copán. During the reign of its 14th ruler, in the eighth century Quiriguá and the wider valley flourished after a violent break with Copán. This was quickly followed by a rapid decline in population density and size. By the end of ninth century Quiriguá was abandoned as were many wider valley sites. This developmental trajectory is reflected in neighboring zones.

**Cacaulapa Valley**

Located 10 km southwest of La Sierra within Urban and Schortman’s Naco Zone (1988), the Cacaulapa Valley is narrowly bounded by the steep sedimentary hills rising 500 to 600 m of the Sierra de Omoa and Sierra de Pija mountain ranges which both run north to south (McFarlane 2005:47, Wells, 2003). Running through the valley’s center the Cacaulapa River carves out narrow corridor linking the Middle Chamelecón and Ulúa drainages (Wells 2003:77). Apart from the Cacaulapa River the valley is watered by the Quebrada La Coyota and the Quebrada Seca, which join the Cacaulapa just east of El Coyote (Figure 2.4).

Two independent surveys have been carried out in and around the valley: (1) from 1969-1974 a geological survey by the United Nations Development Programme (1974); (2) from 1976 to 1979 a subsequent survey was conducted by the Metal Mining Agency of Japan (1979). These studies found that the geological foundation of the valley is composed of the Minitas formation (Paleozoic gneissose, micaceous schist, metamorphosed andesite and tuff) and the Atima formation (limestone). South of El Coyote, the area is covered by the Matagalpa formation (volcanic andesite, basalt,
basaltic pyroclastic rock, and rhyolite). Additionally intrusions of tuff, limestone, granodiorite, andesite, and quartz diorite were found near El Coyote.

The soil composition surrounding El Coyote is known from USGS soil maps and selective pH testing by Wells (2003:80). The upland soils are neutral to mildly acidic clayey to sandy or gravelly loam with relatively good drainage and more representative of the mountain valley soils (McFarlane 2005:49; Wells 2003, 2004). Bottomland soils are silty to sandy loams that are mildly alkaline with good drainage (McFarlane 2005; Wells 2003, 2004). Unlike the neighboring Naco Valley, agriculturally productive land in the Lower Cacaulapa Valley is scarce, limited to a total of 7 km². This is found in patches of discontinuous floodplain none of which reach a meter in width (Wells 2003). Despite the scarcity of arable land El Coyote was constructed one of the largest segments of level and productive land in valley (Urban et al. 1999:20).

Like the Naco Valley and much of northwestern Honduras the Cacaulapa Valley experiences a dry season from February to May and rainy season from late May to January. Annual precipitation averages 1300 mm, which while low for northwestern Honduras is still sufficient to support two agricultural harvests (Andrade 1990). Temperatures during the dry season can reach 35 °C with predictable oscillations characterized by mild mornings and hot afternoons. The rainy season temperature rarely reaches 30 °C with cool humid mornings and warm afternoons, daily sun showers are frequent as are thunderstorms (McFarlane 2005:50-51).
Cultural History. While evidence for the wider valley prior to the Classic period is unknown radiocarbon and ceramic evidence indicates that El Coyote was an important center of social, ritual and economic activity for over a millennium (200 BC – AD 1200) (McFarlane 2005:83). The earliest occupation at El Coyote is evidenced by scattered distribution of Preclassic vessel forms and other material data, on the terrace where the Classic period architecture of El Coyote was subsequently built (see McFarlane 2005).

Ranging from artifact scatters and clusters of cobble arrangements to stone-face platforms a total of 39 sites have been identified in an area of approximately 6 km² along the Cacaulapa River and its adjoining tributaries (see Urban et al. 1999:Table 1).
The architectural data suggests a three-tiered settlement hierarchy and while it is unclear how many sites were contemporary the bulk of the datable sites contain Late Classic assemblages. Ten times any valley contemporaries; El Coyote represents the bulk of monumental architecture in the valley.

Much like sites in the aforementioned valleys, El Coyote exhibits a pronounced growth in population during the Late Classic (ca. AD 600) coeval with monumental construction and political centralization (Wells 2003; McFarlane 2005). Archaeological data indicates that much like its previously mentioned contemporary extra valley sites El Coyote was a regionally autonomous polity during the Late and Terminal Classic (here, AD 600-1000). Wells (2003) suggests that much like the La Sierra in the Naco Valley this development is a response to the development of neighboring state-level societies like Quiriguá and Copán (Schortman and Urban 1996). This is supported by El Coyote’s location on the most productive land in the valley, which would make its elite population reliant on interregional exchange (Wells 2003:68). This interregional interaction is further supported by the core’s site plan, which mimics the lowland Maya (Ashmore 1991, Ashmore and Sabloff 2002).

Occupation continues into the Early Postclassic as evidenced by ceramics recovered from the Northeast Complex (McFarlane 2005). This aggregate of structures also departs from the Late Classic settlement plan of El Coyote.

**Neighboring Zones**

There are five “zones” in southeast Mesoamerica as described by Urban and Schortman (1988). These zones are defined by the distribution of material traits in the greater southeast (see Urban and Schortman 1988:Table 2). This area is important in
understanding the cultural setting from which the material discussed in this thesis is derived. These zones are not discrete cultural entities and they are best discussed in reference as interaction networks. The following is an abridged version of the cultural setting of these zones with focus on the Classic period.

**Western Honduran Highlands.** The highland zone is located in western Honduras and includes the valleys of Copán, La Venta, and La Florida (together “La Entrada Region”, see Aoyama 1994; Wells 2003) and the Middle Ulúa drainage. Like the aforementioned areas of the southeast the western Honduran Highlands experienced slow growth during the Preclassic (Nakamura 1987, 1997; Nakamura et al. 1991) with increased growth in the Early Classic, punctuated by Late Classic expansion and finally Terminal Classic to Postclassic population decrease.

During the Early Classic the Classic Maya Center of Copán emerged as the strongest power in the area. A monument at Copán records the arrival of the dynastic founder, K’ nich Yax K’uk Mo (Great Sun, Green Quetzal Macaw), on February 9, AD 427 (8.19.11.0.13.5 Ben 11 Muan), from a sacred location in the west (probably the Maya Lowlands or Highlands; see Buikstra et al. 2004). With the ascension of its first Ruler Copán rapidly developed the hallmarks of Classic Maya society (see Webster 1988; Fash and Sharer 1991) and the wider valley became increasingly complex and diverse (Fash 2001).

At this time other sites in La Entrada rose to prominence as well (e.g., Las Pilas, El Puente, El Abra, Los Higos, Las Tapias, Gualjoquito) and participated in trade across the Quiriguá-Copán exchange network (Schortman and Nakamura 1991:317). Like Lower Motagua Valley site relationships with Quiriguá these sites show variant
affiliation with Copán as evidenced by the material record. Sites here maintain a common ceramic inventory with Usulután red-painted ceramics as well as utilitarian ceramics throughout the Classic. Late Classic polychromes include locally produced (at Copán) Copador and imported Ulúa polychromes. What is very different however, is the frequency of tenoned façade sculpture, which is rare in the LMV, and hieroglyphic texts, which are absent outside of Quiriguá in the LMV.

The Copán state continued to flourish into the Late Classic and reached it apogee during this period. The aforementioned capture and beheading of Copán’s 13th Ruler by Quiriguá’s 14th Ruler marked a change in the exchange system between this region and Quiriguá and the Lower Motagua Valley. While some items (i.e., obsidian) continued to be traded, fine-ware ceramics (i.e., Copador) exchange seemingly ceased. Copán also renewed ties with groups in El Salvador and strengthened links with groups in the Ulúa region (see Beaudry 1987). Due to a number of factors the Copán polity collapsed in the mid-9th century. Fash (2001:174) gives a three-fold reasoning for Copán’s sociopolitical breakdown “the decentralization of powering during the early eighth and ninth centuries AD, collapse of Copán kingship in AD 822, and the demographic decline of the supporting population and ecological deterioration of the Copán Valley.” By the early 10th century Copán and the surrounding area experience a significant drop in population coinciding with a change in material inventories and household organization (Wells 2003).

Lower Ulúa Valley-Sula Plain. Located in north-central Honduras this area contains some of the most productive agricultural land in Mesoamerica (Wells 2003:49). The region is defined by the Ulúa River, which flows north to its terminus at the
Caribbean Sea, creating a vast floodplain, known as the Sula Plain. This area experienced the same demographic trajectory as other regions in southeast Mesoamerica, although it is more difficult to document archaeologically here. The Early Classic is particularly difficult to identify as many Early Classic sites have Late Classic components (Joyce 1991).

During the Late Classic the region experienced the ubiquitous population growth of the wider southeast region. Several large centers (i.e., La Guacamaya, Villanueva, Calabazas, Currusté, and Travesía) are distributed more or less evenly throughout the valley (Joyce 1991; Luke and Tykot 2007). The political picture of the Ulúa Valley-Sula Plain is less clear than that of other regions, while some have postulated that Travesía was the area’s paramount (Sheehy 1978; Stone 1940), others promote the idea that no one polity had more influence in the valley than another (Henderson and Joyce 2000; Joyce and Sheptak 1983; Luke and Tykot 2007; Luke et al. 2006). In either case the extra-valley ties of Travesía are evidenced by the presence of Ulúa style marble vases throughout the Maya Lowlands and into Lower Central America. It is interesting to note that with only two exceptions El Abra, (Nakamura 1987), and Palos Blancos, (Davis-Salazar and Wells 2007) Ulúa style marble vases are not found to the west of the valley (Luke and Tykot 2007). Turning to ceramics, bold geometric polychromes are abundant, Usulután bowls are common, while Copador is rare to absent from assemblages (Urban and Schortman 1988:246-247). Towards the end of the Classic Period Travesía is abandoned perhaps in favor of the hilltop site of Cerro Palenque at the convergence of the Ulúa, Comayagua and Blanco Rivers (Joyce 1986, 1988, 1991).
A demographic decentralization at Cerro Palenque occurs around AD 1000, possibly due to a convergence of issues chiefly the breakdown of communication networks (see Joyce 1991:146). This Terminal Classic/Early Postclassic phenomena occurs all across southeast Mesoamerica and is demonstrative of just how interconnected and codependent these polities (particularly their elite populations) were.

**Lake Yojoa-Comayagua Valley.** While this area is geographically part of the highlands it shares many characteristics of the Sula Plain (Urban and Schortman 1988). This region experiences marked population growth with the emergence of large ceremonial centers beginning in the Early Classic and continuing into the Late Classic. The largest of these centers were Los Naranjos and Yarumela located in the Yojoa basin and Comayagua Valley respectively. Sites from the Late Classic tend to be on high ground along major rivers and streams with good drainage, agricultural land, and year-long potable water (Agurcia Fasquelle 1986). One notable exception is the Comayagua hilltop site of Tanampua, whose location was possibly chosen for its defensive advantages (Agurcia Fasquelle 1986). As with the previously discussed regions large polities like Yarumela and Los Naranjos collapsed at the end of the Classic Period and were replaced by smaller civic-ceremonial precincts (Hirth 1988:320).

Both the Yojoa-Comayagua and Sula contain regular distributions of Ulúa-Yojoa polychromes with consistency in the diversity of forms and designs. Bold geometric polychromes are also plentiful. Chilanga Red-Painted Usulután vessels as well as Copador are rare to absent in this region. Ceramic imitations of Ulúa style marble vases are found in the Yojoa-Comayaga region and Stone (1957:15) identified a fragment of a Ulúa marble vessel at Yarmumela. Both the Yojoa-Comayagua and Sula regions contain
stone monuments, which based on their general form and vertical orientation resemble stelae used by the Maya to the west (Hirth 1988:311). Many of these monuments are unworked monoliths but there are examples of bas-relief carving, engraved and stucco painted surfaces (Hirth 1988). Sculptured stone is found in the form of tenoned serpent heads at Los Naranjos (Strong et al. 1938) and Cerro Palenque (Joyce 1985), “goggle-eyed grotesque” engraved monuments at Travesía (Stone 1941) and Cerro Palenque (Joyce 1985), and bas-relief scroll-work motifs at Yarumela (Stone 1957; Hirth 1988:311-313). It is of interest that while these regions were certainly in contact with their Maya neighbors to the west (i.e., Copán and Quiriguá) evidenced by Ixtepeque obsidian (Hirth 1988), they deviate from southeast Maya material culture in a number of ways. First the Copador while abundant in El Salvador and eastern Guatemala sites, are rare in the Yojoa-Comayagua region and almost absent from the Sula Plain. Second the absence of Ulúa-Yojoa polychromes and Ulúa style marble vases in assemblages of their (Western Honduran Highlands, Naco Valley, and Lower Motagua Valley), and their presence elsewhere in the Maya Lowlands suggests that interaction along the coast was more important (see Hirth 1988; Joyce 1985). Hirth (1988) points out that Early Classic ceramics of Copán lack the complex Maya iconography present in contemporary Ulúa polychromes, further promoting the coastal communication route hypothesis.
In this chapter, I discuss previous work done in both geochemical provenance and prospection in archaeology. In the first section, I provide an overview of geochemical provenance studies conducted on materials from southeast Mesoamerica, beginning with those concerned with provenance and ending with those investigating prospection. I discuss previous studies using pXRF for both provenance and prospection in the second section. In the final section, I discuss pXRF instrumentation, how the procedure works, its benefits and limitations, and issues of accuracy and precision.

**Geochemical Provenance Studies on Southeast Mesoamerican Archaeological Materials**

Research into artifact provenance involves the use of particular artifact traits to discern an artifact’s point of manufacture or the source of the raw material(s) composing it (Malainey 2011:169) has long been of interest to archaeologists. Identifying an artifact’s procurement and/or production origin is critical in understanding distribution and exchange successfully (Rice 1987). Traditionally, noting the spatial distribution of the artifact type and applying a gravity model is used determine provenance. In this model the area of highest abundance is determined to be the artifact type’s locus of manufacture (Rice 1987).

Another method that has grown in popularity since the 1950s is the physiochemical approach, whose methods are wide and varied. The effort to link artifacts
to sources through compositional analysis depends on the ‘provenance postulate’ (Glascock and Neff 2003; Price 1987; Rands and Bishop 1980; Weigand et al. 1977). The provenance postulate assumes that the raw material source can be successfully determined analytically as long as between source differences are greater than within source differences (Bishop et al. 1980).

Compositional studies of southeast Mesoamerican archaeological material have been employed for the purpose of attributing provenance to a variety of materials including obsidian (e.g., Glascock et al. 1991; Nazaroff et al. 2010; Sheets et al. 1990; Stross et al. 1983) ceramics (e.g., Bishop et al. 1986; Neff et al. 1999; Reents-Budet et al. 2004), stucco pigments (Goodall et al. 2009) and marble (Luke & Tykot 2002, 2007; Luke et al. 2006). These studies conducted on obsidian and ceramics used instrumental neutron activation analysis, stable isotopes were used on marble, while Micro-Raman spectroscopy was employed as an analytical tool on painted stucco fragments.

The oldest and most widely used method of determining provenance of Mesoamerican artifacts geochemically is INAA. This analytical technique gained popularity in archaeology during the 1970s and 1980s in determining sources for pottery, obsidian, chert and other materials (e.g., Hughes et al. 1991; Kuleff and Djingova 1990; Neff and Glascock 1995) and by the 1990s was regarded as the ideal method for provenance research (Bishop et al. 1990). Used as one of the lines of evidence of communication between residents of distant centers, INAA can be an effective tool in interpreting patterns of interaction that can inform on questions of political and economic history, craft production and exchange, and the use of foreign symbols in the consolidation and maintenance of political control (Reents-Budet et al. 2004). Neutron
activation analysis determines elemental composition through the conversion of stable (non-radioactive) atoms into radioactive isotopes. Unstable radionucleotides decay emitting gamma rays whose frequencies are characteristic of the element. This involves the destruction of a powdered sample (30 mg to a few grams) of the artifact. The samples are subjected to neutron irradiation in a nuclear reactor where they are converted to radioactive isotopes.

**Obsidian.** The geochemical provenance of obsidian artifacts has long been of interest to the archaeological community of Mesoamerica. Obsidian artifacts from Mesoamerica have been analyzed with INAA, laboratory XRF, and pXRF. The earliest of these studies to deal with southeast Mesoamerican material discusses obsidian sources as well as artifacts from Quiriguá (Stross et al. 1983). This study shows that XRF and INAA data, while not directly comparable, both are able to attribute obsidian artifacts to their geological provenance. As visual analysis and more recent chemical studies suggest, Stross and colleagues (1983) correctly attribute the vast majority of Quiriguá obsidian samples to Ixtepeque, a widely traded source. This study also attributed one artifact to the El Chayal source group, which was an important source for sites in the coastal Maya Lowlands of modern Belize. This is to be expected as interaction between the LMV and this region is noted in the material record (Urban and Schortman; 1988). Subsequent studies of obsidian have made use of both analytical techniques as well as “visual” sourcing for the purposes of reconstructing long-distance relationships in Mesoamerica (e.g., Aoyama 1994, 2001; Aoyama et al. 1999; Asaro et al. 1978; Braswell et al. 2000; Fowler et al. 1989; Hammond et al. 1984; Harbottle et al. 1994; Glascock et al. 1991;

Of the geochemical provenance studies performed on obsidian, Stross (et al. 1983), Aoyama (1994, 2001; et al. 1999), Braswell (et al. 2000), Harbottle (et al. 1994) Glascock (et al. 1991), and Sheets (et al. 1990) concentrate on collections from the southeast. No southeast obsidian source had been chemically identified before Sheets (et al. 1990), while subsequent studies (see Aoyama et al. 2001; Glascock et al. 1991) added several more sources for the southeast.

The studies of Aoyama (1994, et al. 1999), Braswell (et al. 2001) and Glascock (et al. 1991) report on southeast Mesoamerican material from the Proyecto Arqueológico La Entrada (PALE). One hundred artifacts from 29 archaeological sites of the PALE survey were selected for INAA analysis. Visual analysis was subsequently performed on 34,004 obsidian artifacts from the Copán Valley and its hinterland (Aoyama 2001, this total includes PALE artifacts). Visual sourcing was shown to have a 98 percent success rate (Aoyama 2001) when compared to the original INAA study (Glascock et al. 1991). Aoyama also collected obsidian from known sources including Ixtepeque, El Chayal, San Martín Jilotepeque in Guatemala and La Esperanza and Güinope in Honduras for the original study in 1991. The five sources analyzed were shown to be highly homogeneous (Glascock et al. 1991) and comparable to previous studies done elsewhere in the Maya area (e.g., Stross et al. 1983; Rice et al. 1985) as well as Güinope and La Esperanza sources in central Honduras (Sheets et al. 1990). The majority these of the PALE obsidian artifacts (61 percent INAA) chemically group to the Ixtepeque source in Guatemala, which is hypothesized to be under control of Copán (e.g., Aoyama 1999;
Takeshi and Aoyama 1996; Glascock et al. 1991; Urban and Schortman 1988). Another important source in the PALE assemblage is San Luis (25 percent of INAA) (formerly source X; see Aoyama 1999; Glascock et al. 1991). Temporally there is a rise in the frequency of Ixtepeque obsidian corresponding with the developmental trajectory of Copán, which peaks in the Late Classic. Although Ixtepeque is the dominant source in Copán and the southern La Entrada region it is interesting to note that San Luis/Source Y (presumably a local Honduran source) account for the majority of the of samples in the further north. This “border” of Copán’s influence is also supported by the absence of Copador in northern La Entrada assemblages (Aoyama 1999:247).

A large study was conducted on examples collected from Copán (Harbottle et al. 1994). The chemical results found only seven non-Ixtepeque (of 139 samples) specimens at Copán and all of which group to El Chayal. This is no surprise as it has long been postulated that Copán was a main hub for Ixtepeque obsidian polyhedral core distribution into the southeast (Urban and Schortman 1988). In 2009, I performed visual analysis based on Aoyama’s (1999:Table 2) criterion on obsidian sources found in the La Entrada region on material from Ostuman, a site Copán’s hinterland (about 5 miles from the site core) and attributed 96 percent of the collection to Ixtepeque and the remainder to El Chayal except for one green obsidian example attributed to Pachuca (McCormick, 2009).

Three analytical methods used on obsidian samples from Honduras (123), Nicaragua (12 artifacts, 2 possible source materials) and Costa Rica (4) are reported in Sheets et al. (1990). The Honduran samples were subjected to particle induced X-ray emission at Western Michigan University, while the Costa Rican and Nicaraguan samples were analyzed with both INAA and XRF at the Lawrence Berkeley Laboratory,
University of California. The Honduran samples come from the El Cajón region and show that Güinope and La Esperanza obsidian were important sources during the Classic Period (compare Hirth 1988:Tables 2 and 3; Sheets et al. 1990:149). Throughout the Classic Period this region relies on imported polyhedral cores and finished prismatic blades (from Ixtepeque 70 percent, La Esperanza 25 percent, and El Chayal 2 percent) while relying primarily on Honduran sources for simple flakes and percussion tools (Ixtepeque 4 percent, La Esperanza 38 percent, El Chayal 3 percent, Güinope 30 percent, and 8 percent from an unknown source; see Hirth 1988 for discussion). Sheets et al. (1990) point out that Güinope may be underrepresented, as the unknown source is chemically similar. All of the Costa Rican and Nicaraguan samples were analyzed with XRF and 16 of them were subsequently analyzed with INAA as well. The XRF source attribution of all 14 artifacts were confirmed by INAA and reveal that Ixtepeque, San Martín Jilotepeque, Güinope and a fourth unknown (possibly Nicaraguan source) are found in Costa Rican sites. All these sources are represented in the Nicaraguan assemblage except San Martín Jilotepeque (see Sheets et al. 1990:Table 9). The presence of Guatemalan and Honduran obsidian hundreds of kilometers from their quarries shows some level of interaction was occurring between distant sites.

**Ceramics.** One of the largest and most comprehensive INAA characterization studies is the Maya Polychrome Ceramics Project, which includes a generous amount of material from southeast Mesoamerica. The project was developed to investigate Classic Period Maya painted pottery production, combining chemical and art historical analyses to distinguish styles of Classic ceramics and suggest locales for their manufacture (see Rands and Bishop 1980; Reents-Budet et al. 1994, 2004). The methodology and results of
much of the work outside of the southeast are discussed by Sabloff (et al. 1982) and by Bishop and Beaudry (1994) on materials from the southeast particularly Copán.

The first report concerned with southeast Mesoamerican material is presented by Bishop and colleagues (1986), and discusses the results of a large interregional study on Copador and other cream paste ceramics of the Usulután tradition (see Demarest and Sharer 1982) using INAA to test hypotheses on the production and distribution of these ceramic types. Samples were taken from sites in three archaeological zones: the Rio Copán Zone, the Middle and Lower Motagua Valleys, and Western and West-Central Salvador. This study shows that cream paste ceramics from the Copán zone and El Salvador have a closer chemical correlation than do those from the Motagua (Bishop et al. 1986:164-165). The data suggests that among the ceramics analyzed samples from the Rio Copán zone are primarily of local manufacture, samples from El Salvador group with those found at Copán and another similar source. Specimens from San Agustín Acasaguastlan, in the Middle Motagua Valley, group with Copán, while material from Quiriguá does not. This study suggests at least three sources for Copador and related pottery manufacture, the first being Copán, the second being not far from Copán and a third unknown manufacturing site.

In 1994, Bishop and Beaudry released a more comprehensive report on the results of INAA analyses conducted on ceramics with a focus on material from Copán and other sites in the southeast. This reports the continued efforts of the Bishop et al. (1986) study by expanding the data set to include materials from sites in the Lake Yojoa-Comayagua region, the Naco Valley, and a number of other sites in the western Honduran Highlands (as described in Chapter 2). The results of this comprehensive study give insight into
Copán’s affiliation with other groups in the southeast as well as their ties to centers in the Petén and the Yucatán (see Bishop and Beaudry 1994:424-429).

In 2004 Reents-Budet and colleagues discuss the results of INAA assays conducted on material from four tombs from the Copán acropolis dating to the Early Classic. This study also displays the results of data analysis of material (Reents-Budet et al. 2004, Figures. 9.1-9.4) from the Maya Polychrome Ceramics Project and discusses interpretations of the data. The three tombs represent a timeline of Early Classic elite burials (see Bell et al. 2004) beginning presumably with that of the city’s dynastic founder, K’inch Yak K’uk’ Mo’. The analyses of the INAA attribute the vessels found in these burials to various manufacturing regions (provenance): Copán region, Lower Motagua Valley/Quiriguá, Mexican Highlands, the Petén, the Guatemalan Highlands, and some specimens are given and indeterminate or no attribution. While the largest group in all burials, except one, is that of local manufacture, the amounts of material of imported origin fluctuates through time suggesting differential affiliation of these individuals to the aforementioned regions (see Reents-Budet et al. 2004:188-190). While the earlier burials keep to a wide interregional scope, most of the ceramics from the Sub-Jaguar tomb (the most recent temporally) are attributable to Quiriguá, suggesting the importance of ties between these two polities, ca. 550 AD (Bell et al. 2004b:152).

**Marble.** An important study using stable isotope analyses to chemically identify marble vases and their potential sources was carried out by Luke and colleagues (Luke and Tykot 2002, 2007; Luke et al. 2006) on material from the Late Classic and currently known quarries in the Ulúa Valley of northwestern Honduras. Marble studies in the Mediterranean have shown chemical characteristics may be unique to individual marble
sources, which allows specific artifacts to be attributed to their sources (see Luke and Tykot 2002; Herz 1992; True and Podany 1990; Waelkens et al. 1992). The ideal method for geochemically attributing marble with minimal destruction is stable isotope analysis (Luke and Tykot 2002). The results demonstrate what previous scholars inferred (Gordon 1920, 1921; Kidder 1947; Hirth 1988) without the chemical data, that production of this specific white stone vase style must have been centered in the Ulúa Valley, specifically the site of Travesía (Luke and Tykot 2002; Luke et al. 2006). Ulúa vases have been found throughout the Ulúa Valley, as far north as the central Maya lowlands and as far south modern day Costa Rica. Context and associated artifacts suggest these were a prestige good and their presence in assemblages indicate communication between elites of the Ulúa and far flung centers (see Luke & Tykot 2002, 2007; Luke et al. 2006). In this study the chemical and stylistic analysis is able to tease out the changing dynamics of the Ulúa Valley’s extra-valley political and socioeconomic networks.

Samples were taken from marble sources within the valley and then compared with a corpus (69) of Ulúa style vases (both provenienced and unprovenienced). The results show that the vast majority of Ulúa vases, 84 percent (56) come from the same source throughout the production period (Luke and Tykot 2007; Luke et al. 2006). A second source (possibly a secondary procurement area within the first source) is indicated for 12 percent (8), and 4 percent (2) were attributed to a third source (Luke and Tykot 2007; Luke et al. 2006). These results show a clear preference to one source and that other two sources were exploited in antiquity. Limited stylistic variability and similar isotope analyses for both the procurement zones and vases suggest a single production site. The stylistic and distributional data indicate that workshop demands may have
expanded raw material extraction to include additional quarries during the end of the Late Classic into the Terminal Classic.

**Geochemical Prospection on Southeast Mesoamerican Archaeological Materials**

The application of geochemical methods in archaeology have been used to locate and characterize archaeological sites and human activity areas, study practices of land use, and explain archaeological features (Oonk et al. 2009:35). These include studies of archaeological floors and surfaces made from soils and plasters. A number of compositional studies have been conducted in southeast Mesoamerica on both types of materials. These studies have been primarily conducted on soil, and use a variety of methods (Canuto 2002; Canuto et al. 2010; Parnell et al. 2002), including inductively coupled plasma-mass spectrometry (ICP-MS) to investigate activity areas (Rothenberg 2010; Wells 2003, Wells et al 2007).

Beyond the southeast, in Mesoamerica a number of scholars (e.g., Abrams et al. 2012; Barba 2010, 1986; Barba and Ortiz 1992; Barba et al. 1996, 2007; Cook et al. 2006; Hutson and Terry 2006; Parnell et al. 2002a, 2002b; Pecci et al. 2010; Terry et al. 2000, 2004; Wells 2000) have conducted chemical studies of plaster in both archaeological and ethnohistorical settings. The composition of these floors is largely lime-based (calcium carbonate), a chalky surface known to accumulate and preserve a variety of chemical compounds overtime (Barba 1986). While various studies have been conducted on both soils and plaster to investigate activity patterns, all the methods to date are destructive.
Geochemical compositional studies of space-use patterns are important to the interpretation of archaeological sites because they add another layer of data indicative of ancient activity. Traditional methods relied almost exclusively on artifact distribution; this can be misleading due to the poor preservation or disturbance of material (Manzanilla and Barba 1990). Artifacts can and often are removed from the loci of activity before deposition; but in many cases chemical signatures can indicate specific activity that can become fixed to surfaces where the activity took place (Parnell et al. 2002a).

The earliest study to make use of geochemical prospection in southeast Mesoamerica is reported in Parnell et al. (2002a) and investigates soils at the Classic Maya center of Cerén, El Salvador. Investigation of activity areas at this site are of particular interest as Cerén was covered and preserved with volcanic ash around AD 600 (Sheets et al. 1990) thus allowing analysis of soils associated with known activity areas to a degree not usually possible (Parnell et al. 2002a). This study utilized two methods to investigate different chemical residues: (1) weak acid extraction of phosphate (see Terry et al. 2000 for discussion) and (2) DTPA (diethylenetriaminepentaacetic acid) extraction for heavy metals (see Lindsay and Norvell 1978; Parnell et al. 2002b for discussion). The chemical methods were employed to soils gathered from excavations within a specific locus at Cerén, structure 10, as this building was of ritual significance (see Parnell et al. 2002a; Brown and Sheets 2001 for discussion). The results of phosphorus extraction showed that the area south of the building were high in phosphorus, which supported its identification as a midden where food and other organic phosphate bearing materials are deposited (Parnell et al. 2002a, 2002b). DTPA extraction found iron in both the midden
(south) and the east room of structure 10, which may be a function of red hematite noted on interior walls and the butchering of deer within the structure (Parnell et al. 2002a:338). Samples from the east room also found mercury and other heavy metals (copper, manganese, lead, and zinc) in the same area as the high iron concentrations. The heavy metals are seen to be a function of the pigments (cinnabar) and paints (red hematite) found in the room.

Wells (2004) investigated the site of El Coyote using ICP-AES to obtain multi-elemental characterizations of sediments from plaza spaces. Samples discussed in this work come from excavations conducted around the main plaza, a lime-plastered surface approximately 107 m (north-south) by 51 m (east-west) (Wells 2004:69). As artifacts patterns indicate that plaza debris was probably transported to secondary locations (namely middens), soil characterization of plaza deposits is crucial to understanding ancient activity patterns at El Coyote (Wells 2004). Samples from excavation contexts were gathered from both inside and outside the plaza (see Wells 2003, 2004 for detail) and subjected to ICP-AES analysis to determine elemental concentrations of a suite of elements (aluminum, calcium, iron, potassium, magnesium, sodium, phosphorus, strontium, zinc, manganese, and titanium). The elemental data was used to model concentrations of elements indicative of human activity (Wells 2004:Figures 2-4). Here the results of ICP-AES analysis and excavated artifacts were used to identify and interpret three types of soils in and around the main plaza at El Coyote and assign ancient activities to each soil type. Group I soils (NW corner, outside plaza) were interpreted to indicate areas associated with craft production as they had low concentrations of potassium (K) and phosphorus (P) (elements indicative of food production) and evidence
of craft production. Soils in the interior of plazas (both main, and southern groups) were classified as group II, indicative of ritual behavior with high concentrations of P and low concentrations of K. Middens and domestic activity areas comprise group III (east middens), as these soils have elevated levels of P and the lowest levels of K.

Wells and colleagues (2007) present thorough synopses of ethnoarchaeological studies conducted throughout Mesoamerica (Barba 1992; Barba and Denise 1984; Barba et al. 1995; Fernandez et al. 2002; Middleton et al. 1996; Middleton 2004; Wells 2003, 2004) and provide an archaeological case study as well. Comparison of the ethnoarchaeological studies allowed Wells et al. (2007) to make a number of generalizations about the chemical signatures left behind by various human, generally food related activities (see Wells et al. 2007:Table 1). This study found that soils in food preparation areas involved in cooking are low in phosphates, while areas near cooking areas are high in phosphates. This is postulated as a result of the deposition of wood ash from cooking fires, which prevents P from adhering to sediments. This ash leaves its own chemical signature, namely high concentrations of K and Mg. So K and Mg levels corresponding with ash deposition can be used in conjunction with P level distribution can be used to identify cooking areas. This hypothesis is tested by sampling ancient hearths, ovens, and surrounding floor spaces from Palmarejo, Honduras and processing the samples using ICP-MS (see Wells 2004; Wells et al. 2007). The elemental data was then scrutinized using principal components analysis. Results of this statistical endeavor showed that hearths exhibit high levels of K and Mg and that Na, Ba, and Fe may be useful in distinguishing hearths from ovens. Scrutinization of the elemental data by discriminant function investigated the ancient activity patterns of a civic ceremonial plaza.
and elite patio at Palmarejo, which allowed inferences to be made as to how different parts of each space were used (see Wells et al. 2007:Figures. 5-6). The discriminant function scores were also visualized using Kriging software, which permitted the distribution of P and Factor Score 1 to be displayed with relation to the spaces being examined (see Wells et al. 2007:6-7).

Rothenberg (2010) follows the same methodology used in Wells et al. (2007) employing pH, P testing, and ICP-AES to investigate activity patterns at the north plaza of Palmarejo. According to Rothenberg’s (2010) analysis the Palmarejo north plaza’s space-use pattern conforms to the civic ceremonial plaza and differs from the patio group discussed in Wells et al. (2007). This conclusion was reached by using a combination of chemical data and artifacts excavated from the plaza.

In 2010 Canuto and colleagues utilized phosphorus analysis to compare space use at two centers in the El Paraíso valley in western Honduras. Both soil and plaster floors were analyzed using the Mehlich 2 weak acid extraction procedure (see, Terry et al. 2000) at Yale University. The two sites under investigation were El Cafetal (11 samples) and El Paraíso. Results from analyses conducted at El Cafetal were consistent with results at El Coyote (Canuto et al. 2010; cf. Wells 2004), showing high P concentrations in the middle and southern end of the main plaza suggesting these areas were used for food preparation and feasting. A combination of excavated materials and P-levels were used to suggest space use for areas at El Cafetal’s main plaza and northern plaza. El Paraíso space-use patterns contrast with El Cafetal’s. Here material from three patios were analyzed, two of them being spaces of ritual-ceremonial use with plastered floors (patios 1 & 3) and one being a “back-yard” for the disposal of residential refuse (patio 2, Canuto
et al. 2010:36-37). High P levels occur in the southern and central areas of patios 1 and 3, consistent with El Cafetal and El Coyote but do not occur at the northern area of patio 2. This is consistent with patios 1 and 3 being public and patio 2 not. The P levels at each site have interesting implications for the uses of each space. Canuto et al. (2010) suggest that the relatively lower concentrations of P at El Paraíso patios 1 and 3 when compared to El Cafetal’s main and northern plazas suggest that these patios were regularly cleaned after activity. The high P levels in the main plaza at El Cafetal suggest the opposite but may also be a function of the non-plastered surface at this site being harder to clean (Canuto et al. 2010:38). Whatever the case, Canuto et al. (2010) conclude that patio usage at these two sites were inherently different with more diverse and inclusive activities being conducted at El Cafetal and less diverse and exclusive activities occurring at El Paraíso. This is seen as a function of cultural differences between the two sites El Paraíso being more like other Maya centers (particularly Copán) in their use of space and El Cafetal more akin to non-Maya sites in western Honduras (i.e., Coyote, Sula Plain, Naco Valley; see Canuto 2002; Canuto et al. 2010).

Provenance and Prospection: Potentials of PXRF

PXRF – How It Works. Portable X-ray fluorescence spectrometry is an energy dispersive XRF (EDXRF) technique. It measures concentrations of a suite of elements by use of primary X-rays (from an X-ray tube). Elemental data is gathered when primary X-rays displace electrons from the inner orbits of surface atoms, which are subsequently filled with electrons from the outer orbits releasing energy in the form of a secondary X-ray (fluorescent) that is recognized by a silicon-PIN (Si-PIN) detector. The energy of this
fluorescent X-ray is indicative of the elements present and their concentrations in the sample (Liritzis and Zacharias 2011; Malainey 2011; Pollard et al. 2007).

The contact of a primary X-ray to a sample causes absorption and scattering to take place. Scattering can be elastic (coherent or Rayleigh scattering) or inelastic (incoherent or Compton scattering). In coherent scattering the ray has the same wavelength and energy as the primary beam. Incoherent scattering results in lower energy and longer wavelength X-rays. Generally absorption is the dominant process that occurs when the primary X-ray strikes the sample. It is the absorption of X-rays that causes the ejection of an electron from its orbital shell. This ejection creates inner shell vacancies. These vacancies de-excite releasing energy to as a secondary or fluorescent X-ray (Pollard et al. 2007). Since the relationship between the emission wavelength and atomic number is known, isolation of individual characteristic lines allow for the unique identification of an element. Thus elemental concentrations can be estimated from characteristic line intensities (Liritzis and Zacharias 2011).

There are some key differences between pXRF and traditional XRF that warrant discussion here. The first key difference is that for regular XRF samples are placed inside a sample chamber internal to the instrument. These XRF instruments create a vacuum inside the sample chamber to eliminate background “noise” during analysis. Although pXRF samples are analyzed outside of the instrument an external vacuum generator can by applied for flat samples. Secondly, traditional XRF analysis involves taking a portion of the sample and homogenization by pulverizing into powder. For the vast majority of these analyses no powder samples were made because there was an emphasis to make the experiments non-destructive (but see Analysis section on Plaster, Chapter 4). With any
sample there is potential variability between different parts or areas of that sample. However, other techniques do not homogenize the whole object but only a portion of it. Ceramic samples are often powdered and homogenized for regular XRF analyses, so that there is no issue of surface morphology. This becomes an issue using solid samples with pXRF as a rounded or bumpy surface can leave space between the instrument and the sample, and also because pXRF only penetrates <1mm of the sample depending on the material matrix (Tykot 2012, personal communication). In the experiments discussed in this thesis care was taken to use flat surfaces for assays. To address this potential variability each ceramic sample was assayed twice, once on the inner and once on the outer edge of the sample. Another difference is that pXRF is not as sensitive as regular XRF instruments in gathering elemental data however, pXRF is able to detect concentrations in low parts per million (ppm).

**Benefits and Limitations of pXRF.** The use of pXRF in compositional studies has both its advantages and drawbacks. The distinct advantage of this instrument is in its portability. Since samples are analyzed outside of the instrument size and shape are not restrictive as they would be in regular XRF instruments. This allows for rapid data gathering of museum materials as well as in-situ archaeological features (see Liritzis and Zacharias 2011; Shackley 2011; Davis et al. 2012). Many of the aforementioned studies voice the incomparability of pXRF data with the data produced by other techniques including regular XRF. Essentially analyses performed by different instruments on the same samples do not give directly comparable results. However, all the studies previously discussed found that pXRF data was useful in distinguishing source groups.
The advantage of pXRF’s portability is in its ability to analyze samples in the open air without any restrictions on shape or maximum size. This gives the distinct advantage of minimal sample preparation as specimens do not need to be cut, drilled, etc. before assaying. Artifacts however, should be cleaned, as surface contamination can render misleading information. While open air analysis allows for more flexibility in data gathering it comes with the caveat that any space between the instrument and the sample can potentially cause “background noise” in the data. This can be minimized by analyzing surfaces that are as flat as possible and performing multiple assays on each sample. Samples should also be larger than 5x7 mm in their smallest dimension to cover the entirety of the X-ray beam and greater than 2 mm thick because not covering the X-ray beam or having the X-ray pass through the sample will essentially take readings on the air, which adds to “background noise” (Shackley 2011). Portability also means that analyses can be conducted on-site and ameliorate the bureaucratic procedure of taking materials out of the country of excavation or out of museum collections to off-site laboratories.

Geochemical data can be gathered with a pXRF in a completely non-destructive manner. This is a distinct advantage over traditional laboratory methods as most involve destroying at least part of the sample for analysis (i.e., ICP-MS, INAA), or at least have a small-to-modest size limitation for the sample chamber. Conducting non-destructive analysis also avoids bureaucratic entanglement of getting permission of owners, be they nation-states, museums, cultural groups or private collections to destroy part of the sample. This is especially important in North America as Native American Tribes (United States), First Nations (Canada), and Inuit (United States and Canada) do not allow
destructive analyses to be conducted on any proprietary archaeological material. The
drawback of non-destructive pXRF analysis is that by nature it is a surface analysis
technique and therefore subject to surface morphology and only gathers data on the area
of the sample touching the detector. Destructive analyses of ceramics generally use
samples homogenized powder of the paste matrix. While the latter method has long been
the standard used to address issues of sourcing it carries with it the problems of
necessitating destructive and off-site analysis, which pXRF eliminates.

Another important aspect of all pXRF instruments is the range of elements they
can detect. As discussed above there are many different commercial pXRF instruments
available. Portable XRF instruments have been shown to gather accurate values on a wide
range of elements but have difficulty with low Z elements and detecting concentrations at
low levels. The accuracy varies by material and concentrations therein. All of the issues
mentioned here also vary by instrument. The materials discussed in this thesis were
analyzed with Bruker Tracer III-V and III-SD pXRF instruments capable of performing
simultaneous multi-element analysis in the range of Mg(12) to U(92) (Liritzis and
Zacharias 2011:115). Regardless of the instrument in question the range of analyzable
elements comes with the caveat that data on a limited number of these elements can be
gathered dependent on the settings used at any one time. Certain elements are more
precisely analyzed by one setting than by another and in some cases for a given element
one can be near detection limits for one setting but not by another setting (see Liritzis and
Another important advantage of using pXRF is the fast processing of elemental data. This advantage goes hand-in-hand with its portability and non-destructive abilities. Data is gathered and processed essentially in real-time with minimal sample preparation.

The accuracy of pXRF data is of chief concern in archaeological studies. It is paramount to use settings that have been shown to be useful in gathering data on the elements of interest for the archaeological question. While pXRF has been shown to gather data that is useful on a number of materials (i.e., obsidian, ceramics) to investigate many archaeological questions it has been noted to not be directly comparable to other methods (see discussion above). This can be compensated for with data calibrations so that data can be directly compared.

Portable XRF has been shown to produce precise results in the studies mentioned above comparable to that of other machines. This precision will vary based on the machine (make, model, etc.), the settings used, and the presence or absence of a filter during data gathering in regards to the elements of interest. Although pXRF has been shown to not be as precise for some elements under certain settings as other instruments it nonetheless has shown its ability to elementally characterize material composition.

Above I have discussed both the advantages and disadvantages of pXRF instrumentation in archaeological research. Portable XRF instruments have the ability to gather simultaneous multi-elemental data on a number of materials with satisfactory accuracy and precision to answer archaeological questions. Settings can be adjusted and filters applied to increase precision and accuracy on specific elements pertinent to the question however, increased precision on certain elements may cede precision and/or detectability on others. Its portability gives pXRF the ability to analyze samples of
virtually any size or shape; however, this portability sacrifices the analytical precision of a laboratory instrument, which can gather data on elements at potentially lower detection limits and because it has been around longer has more developed calibration software. Portability also allows for analysis on site whether in the field, museum, etc. and results are available within seconds, unlike traditional methods which require use of off-site equipment, increased sample preparation, and longer data turn around. The overall accuracy and precision of pXRF is not as strong as in traditional laboratory methods. Despite compromised accuracy and precision a number of studies have shown pXRF data can be corrected to compare to data gathered by other methods (e.g., see Glascock 2011; Drake et al. 2009; Nazaroff et al. 2010). When used non-destructively pXRF leaves samples unchanged by analysis, allowing samples to be used for future reference and research. The cost per sample goes down as sample preparation is minimal and instrumentation is less expensive than traditional methods.

**Previous studies using pXRF in Archaeological Provenance Studies.** The use of handheld pXRF instruments has expanded in its use for analysis of archaeological specimens (Shackley 2011; Forster et al. 2011). Of particular interest are investigations conducted in provenance research on obsidian (e.g., Craig et al. 2007, 2010; Drake et al. 2009; Kellett et al. 2013; Nazaroff et al. 2010; Phillips and Speakman 2009; Sheppard et al. 2011; Tykot et al. 2011; Weiming Jia et al. 2010) and ceramics (Burley et al. 2010; Forster et al. 2011; Frankel and Webb 2012; Goren et al. 2011; Johnson 2012; Matsunaga 2009; Morgenstein et al. 2005; Speakman et al. 2011). The pXRF instruments employed in these studies have been manufactured by a variety of companies including Amptek (Craig et al. 2007), Bruker (Craig et al. 2010; Drake et al. 2009; Forster et al. 2011;
Johnson et al. 2012; Nazaroff et al. 2010; Phillips and Speakman 2009; Speakman et al. 2011; Tykot et al. 2011; Weiming Jia et al. 2010); Innov-X (Sheppard et al. 2011); and Niton (Burley et al. 2010; Frankel and Webb 2012; Goren et al. 2011; Matsunaga 2009; Morgenstein et al. 2005). Of all the published studies using pXRF for provenance research only Nazaroff (et al. 2010) and Drake (et al. 2009) deal with material from the Maya area.

**Previous Provenance Studies using pXRF on Obsidian.** Portable XRF has been applied to obsidian provenance research all over the world including the Kuril Islands in Russia (Phillips and Speakman 2009), New Zealand (Sheppard et al. 2011), Peru (Craig et al. 2005, 2007; Kellett et al. 2013), Serbia (Matsunaga 2009), Sardinia (Freund and Tykot 2011; Tykot et al. 2011), China (Weiming Jia et al. 2010) and the Maya Lowlands (Drake et al. 2009; Nazaroff et al. 2010). In each case the goal of these studies has been to document networks of exchange and transport of obsidian from their geological source(s) to their archaeological provenience(s). Many of these investigations use a multi-method approach, employing regular XRF (Craig et al. 2007; Drake 2009; Nazaroff 2010) and ICP-MS (Kellet et al. 2013; Phillips and Speakman 2009; Tykot et al. 2011) with pXRF. The reason for these methodological comparative studies is to see how pXRF measures up against well-established methods of geochemical sourcing.

The earliest comparative study published on obsidian artifacts (Craig et al. 2007) concluded that there was good agreement with numerical elemental data gathered by both instruments. Significant differences did occurred between regular XRF and pXRF with certain Z-elements, and the error rate was noticeably higher giving larger dispersions about the mean in biplots with pXRF data (Craig et al. 2007; Shackley 2011). While
geochemical readings between instruments may not be equivalent, pXRF data can nonetheless distinguish between source clusters (Craig et al. 2007).

Drake et al.’s (2009) comparison of regular and portable XRF concisely illuminates some of the key differences in the analytical capabilities of the two instruments. First this study found that the Bruker Tracer III-V produced geochemical readings for Rb, Sr, Zr and Y, which were consistently 6 percent different than the regular ED-XRF at Berkeley (see Drake et al. 2009:14, 16). The authors concluded that while pXRF numerical data was not as accurate it was indeed precise. Consistent with Craig (et al. 2007), Drake (et al. 2007) found pXRF was deemed useful in distinguishing source groups. Furthermore, by creating a “treatment for the PXRF data, a large amount of error (roughly 6 percent for Rb, Sr, Y, Zr, Y) can be identified and corrected” (Drake et al. 2007:16; emphasis in original).

The investigation of Nazaroff and colleagues (2010) is a more detailed report of the aforementioned article. Fifty-six samples from two sites in Belize, Uxbenká (32) and Ex Xux (24) were analyzed with the regular XRF, while 124 additional samples were assayed with pXRF. All of these samples came from Classic Period contexts. The results from both instruments showed that 7 samples best fit the Ixtepeque group, 47 the El Chayal group, and 1 the Pachuca group. The use of a correction for systematic error between instruments can be used to essentially create directly comparable data (Nazaroff 2010:892). The further analysis of obsidian artifacts (n=180) produced similar results to those analyzed with both instruments, in total 149 were assigned to El Chayal, 24 to Ixtepeque, 2 to Pachuca and 5 were not assigned to any of these three sources. These are
consistent with other sites in this area of the Maya Lowlands where during the Classic Period El Chayal was the dominant source for production of obsidian tools.

Studies on Sardinian obsidian (Freund and Tykot 2011; Tykot et al. 2011) have used pXRF to distinguish source groups from a number of sites. These studies have shown the differential exploitation of various outcrops in Sardinia during the Bronze Age. In both of these studies X-Y scatter plots of Rb/Nb (Y) and Sr/Nb (X) of pXRF data are used to show distribution of artifacts. Freund and Tykot (2011) use pXRF to investigate exchange networks between sites during this period, and discuss the typological (tool type) distribution of obsidian artifacts as to their parent material. Tykot et al. (2011) discuss obsidian artifacts from the Neolithic site of Contraguda in a similar way.

Phillips and Speakman (2009) analyzed 139 samples of obsidian debitage from biface tool production at 18 sites on 8 islands in the Russian Far East. The pXRF data was compared to an INAA database on northeast Asian obsidian to assign possible extant compositional groups. Due to size constraints and ambiguous results six samples were analyzed with laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and compared to INAA data on northeast Asian obsidian (see Phillips and Speakman 2009:1258). The three geochemical methods employed in this study have all been shown to generate comparable data for obsidian (Phillips and Speakman 2009; Speakman and Neff 2005; Speakman et al. 2002). The majority of the samples, which were analyzed with pXRF only, were assigned to known source groups in the area. Results of the samples analyzed with LA-ICP-MS only (6) were inconclusive and were not assigned a
group source and may be attributable to sources outside the immediate area on the mainland of the Russian Far East (Phillips and Speakman 2009:1259).

Ninety-four obsidian artifacts from two recent research projects in Peru were analyzed by Kellett et al. (2013) using both pXRF and LA-ICP-MS. The data produced by both methods were subjected to hierarchical cluster analysis and in both cases produced an identical division of samples into five identifiable source groups (Kellett et al. 2013:15, figures 5, 6a, and 6b). Four of the five clusters produced were reliably sourced to known sources (Kellett et al. 2013).

**Previous Provenance Studies using pXRF on Ceramics.** To date this thesis is the only pXRF provenance study on ceramics from Mesoamerica, however, this method has been applied to various sites in Polynesia (Burley and Dickinson 2010), Turkey (Forster et al. 2011), Cyprus (Frankel and Webb 2012), the ancient Near East (Goren et al. 2012), North Carolina (Johnson 2012), Serbia (Matsunaga 2009), Egypt (Morgenstein and Redmount 2005), the American Southwest (Speakman et al. 2011), and Italy (Terenzi et al. 2010). The results of these and other early studies have been promising for the use of pXRF in ceramic provenience studies as the authors repeatedly have concluded that the data produced is usable in distinguishing between local and non-local wares.

The earliest study published to employ pXRF to study ceramic provenance (Morgenstein and Redmount 2005) used a semi-destructive method of powdering samples for analysis. This study concluded that the instrument used (Niton XLt-783W) is not ideal for ceramic provenance work, because some key elements normally used for such studies cannot be detected (see Morgenstein and Redmount 2005:1616). While this is true of pXRF in general, this statement was made when pXRF ceramic provenance
studies were completely experimental and the elements used in such studies were largely those used in INAA studies, which, by virtue of instrumental difference, gathers data on a different suite of elements. The authors concluded that the elemental data produced were still adequate for sourcing purposes (Morgenstein and Redmount 2005).

Burley and Dickenson (2010) investigated an anomalous subset of pottery in the ceramic sequence of a site in Polynesia through pXRF instrumentation and petrographic analysis. The authors operate under the hypothesis that this subset of ceramics are among the first pots in Polynesia and represent a migration event to the island of Nukuleka, in the Tonga area of Polynesia (see Burley and Dickenson 2010). The inference is based on the amount of pottery found at the site with western Lapita motifs (see Burley and Dickenson 2010:1021). The eastern Lapita style is less decorated and characteristic of Nukuleka and the rest of the Tonga. Previous petrographic studies have shown that western and eastern style wares from Nukuleka differ mineralogically. The geochemical and petrographic differences both point to a non-local origin for western style Lapita ceramics found at Nukuleka and furthermore rule out the possibility that they were produced in the neighboring archipelagoes of Samoa, Lau and Fiji but come from even further west.

Terenzi and colleagues (2010) utilize a combination of geochemical (pXRF) and geophysical (2D proton nuclear magnetic resonance or NMR) methodology in their characterization of Phlegrean ceramics from Cuma and Miseno in southern Italy. The NMR and pXRF analyses were conducted on sixteen ceramic samples spanning eight centuries (ca. 500-1200 AD) from two sites to investigate if these two methodologies can be used in conjunction to provide a description of ceramic manufacturing signature
pXRF and NMR data suggest that the Miseno ceramic assemblage is more homogenous than that of Cuma. These findings are congruent with the excavation data as the Miseno samples were found near the kiln that produced them and no kiln has been identified at Cuma. Comparison was made with a previous study (Grifa et al. 2009) that had established different chemical signatures for cooking ware and table ware at Cuma. A comparison of Fe, Ca, and K showed that while there is intrasite variation in trace elements, the above minor elements are similar in ceramic wares from both sites (Terenzi et al. 2010:1407). This suggests similarity in the technological process of ceramic manufacture at both sites and that ceramics at each site were derived from different raw materials.

Two publications in 2011 (Forster et al. and Speakman et al.) compare data produced with pXRF to those produced with INAA. Both studies found pXRF to be reliable in constructing compositional groups similar to those produced with INAA data. Speakman et al. (2011:Figure 4) show this graphically with results of principal components analysis (PCA) and elemental scatter plots for data produced by both methods on the same sherds. Forster et al. (2010) identified eight compositional groups using both methods for various sites investigated in Turkey. All of the ceramics here were manufactured using local materials, however, the authors identify multiple sources for three of the four sites investigated (Forster et al. 2010:397).

Following a similar methodology as the two studies mentioned above Goren and colleagues (2011) examine the ability of pXRF to distinguish source groups of cuneiform tablets from throughout the Near East and compare these data to those obtained with INAA and petrography. Again the high potential of pXRF data to distinguish source
groups was supported. There is a high degree of agreement between source attributions with all three methods. This remains true regardless of the archaeological provenience of the material as much of it has been shown geochemically and petrographically to have been produced by non-local clays (see Goren et al. 2011).

Frankel and Webb (2012) show that pXRF data can be used to identify chemical differences between the ceramic assemblages of sites as well as identify ceramics made of non-local clay within site assemblages. Elemental data was gathered on four different ceramic assemblages, two of which are from settlements and two from cemeteries. Scatter plots of PCA show that Drab Polished (DP) ware (fine) from both sites are made from non-local sources while most Red Polished (RP) wares (utilitarian) from both sites come from local clay sources. However, fine incised RP from one cemetery context was concluded to be made of non-local material. The authors also concluded that one of the sites made ceramics from two local clay sources (Frankel and Webb 2012:1384).

**Previous Prospection Studies using pXRF.** A paper presented at the 38th International Symposium on Archaeometry conference in Tampa utilized pXRF to investigate human activity patterns (Canuto et al. 2010b). This study presents the results of data gathered with a Innov-X Alpha PXRF analyzer and compares it to data obtained with ICP-MS on the same soil samples from plazas at El Cafetal and El Paraíso. The research was designed to examine if samples with anomalous P values (as recorded through ICP-MS) also had anomalous metal values. Six elements (Ti, Fe, Zn, Rb, Sr and Zr) were consistently found at detectable levels in two patios at El Paraíso. Eight elements (Ti, Mn, Fe, Co, Zn, Rb, Sr & Zr) were consistently found at detectable levels in two patios analyzed at El Cafetal. While the study, actually presented by Richard Lundin,
suggests that pXRF can be used to detect anomalous metal concentrations that correspond to results gathered by ICP-MS, personal communication (2011, 2012) with senior authors Marcello Canuto and Ellen Bell suggest otherwise. Both Canuto and Bell were skeptical of the conclusions reached in this presentation and with good reason. While there is a loose correlation between metal anomalies and P-values, it is unclear how or why this is occurring. To draw inferences about what these correlations mean for ancient activity is challenging.

Recently an accepted manuscript for publication (Gauss et al. 2013) reconstructs prehistoric settlement patterns using pXRF at a Bronze Age settlement in Slovakia. This article used a combination of methods to test the feasibility of using pXRF to investigate chemical signatures in sediments at various depths, against atomic absorption spectroscopy and ICP-OES. Gauss et al. (2013) concluded that pXRF analyses can be reproduced to a high level of accuracy. In this study sediment samples were taken with an auger from three loci (a house with alleys and ditch, a potential metal workshop, and the settlement center) and a percussion drill from one locus (a ditch) of the site and analyzed with the above methods to test for anomalies in their chemical signatures indicative of human activity. Prior to pXRF analysis the samples were dried and homogenized with both ideal and simple sample preparation (see Gauss et al. 2013 for discussion).

Concentrations of calcium, iron, potassium, phosphorus, rubidium, strontium, titanium and zirconium were deemed suitable for statistical analysis. The results showed elevated levels of phosphorus in the ditch and alleys around the house, which is to be expected as these are areas where one expects deposition of waste products and excrement to be high. The house itself showed less phosphorus enrichment but high
concentrations of calcium and strontium, which are consistent with patterns observed by previous studies (see Middleton and Price 1996). The sediments of the potential metal workshop did not contain high levels of copper or tin, which would be indicative of metallurgy, excavations confirmed that this was not a metal workshop. Samples taken with a percussion drill from a ditch at the site enabled the authors to analyze sediments from specific depths. The results of this show give a nuanced chemical history of the anthropogenic inputs that filled the ditch. Originally probably a protective structure the ditch was later filled in with anthropogenic inputs, indicated by increasing concentrations of phosphorus and calcium. The authors conclude that the results of pXRF data and that gathered by other methods are usable in studying human activity patterns in archaeological soils. Particularly pertinent in this study is that a large spectrum of elements currently recognized in human activity pattern studies were shown to be accurately gathered with pXRF instrumentation. The ability to conduct such a survey in the field without having to send material off-site for laboratory analysis is significant.
Chapter 4: Analysis and Results

Due to the nature of this study, this chapter is divided into two sections, one for each of the material classes analyzed. Data was collected using Bruker Tracer III-V and III-SD portable hand held XRF analyzer, equipped with a rhodium tube and peltier cooled Si-PIN detector. This particular model is increasingly utilized in non-destructive archaeological research (Forster 2011; Jia et al. 2010; Phillips and Speakman 2009; Nazaroff 2010). The pXRF spectrometers used in the University of South Florida Laboratory for Archaeological Science have been shown to produce results with repeated precision on a number of international standards and in-house materials.

Provenance Experiments: Ceramics

Research Design. I collected elemental data by non-destructive pXRF assays on a total of 229 sherds from Lower Motagua Valley sites (Quiriguá=72, Playitas=18, Quebradas=12, Comanche Farm=4, Choco=1), 40 from La Sierra, Naco Valley and 82 from El Coyote, Cacaulapa Valley). The material was gathered by three separate projects the QAP (Quiriguá and LMV), NVP and CVP. I performed assays on flat surfaces and took precautions to avoid surface treatments (i.e., paint) on the sample surface as this could render data misrepresentative of the ceramic matrix of the sample. Sample selection differed by valley/project. All available sherds from the non-Quiriguá LMV and CVP were analyzed. The 72 Quiriguá sherds were selected to reflect the type-variety collection, all of the “types” available are represented in this sample. A similar selection
process was implemented with the NVP material. Some samples of interest were unable to be analyzed because of the presence of paint on all of the surfaces. Other samples were only assayed on one surface due to the lack of a second assayable surface (due to paint) on the opposite side, or due to time constraints.

It is important here to note that the assays conducted on the sherds mentioned above were done with three different physical machines. These machines represent two models made by Bruker, the Tracer III-V and III-SD, while in each set of assays the machines were set to the same settings. The majority of the assays were conducted with pXRF's in the University of South Florida Laboratory for Archaeological Science. However, a small subset of 12 sherds was assayed with a Tracer III-V on loan from Bruker to the University of Pennsylvania Museum of Archaeology and Anthropology (hereafter Penn Museum).

The data collection began on July 6, 2010 while the author was interning at the Penn Museum as an exploratory exercise. The settings for the original analysis, which consisted of twenty sherds from Quiriguá were 40kV, 1.5µA, 180 seconds, with no vacuum and no filter, these settings were used throughout the data collection. The Quiriguá sherds are housed in the American Section of the Penn Museum and were provided for study by Dr. Robert Sharer. For this first round of analysis many of the sherds were assayed three times, once each on the inner and outer surface and once on the edge. Assaying of the edges was abandoned in subsequent data gathering as broken edges are more likely to give a less precise reading. The roughness, possibility of dirt contamination and surface area, which was often insufficient to cover the XRF beam (Tykot personal communication 2010) all led to the decision to abandon assaying of
edges and to remove results of edge assays from the statistical analysis. Data collection continued in April 2011 with a pXRF on loan to the conservation department of the Penn Museum with a sample of twelve Quiriguá sherds. In January 2012 a third group of sherds were assayed with the same pXRF instrument as the first group and included 40 Quiriguá, 35 non-Quiriguá LMV, and 40 from La Sierra, Naco Valley. The sherds from the non-Quiriguá LMV and Naco Valley had been previously housed at the home of Dr. Ronald Bishop in Mechanicsville, Maryland and were brought by myself to the Penn Museum where they currently reside. The final assays were conducted by the author with a third pXRF instrument on eighty-two sherds from El Coyote Cacaulapa Valley at the University of South Florida Laboratory for Archaeological Science in December of 2012. These samples were provided by Dr. Christian Wells and are housed at the Mesoamerican Archaeology Laboratory at the University of South Florida. This final data set was done with a Tracer III-SD at the same settings as the previous ones except that the time for these assays was 120 seconds. The change in time of the assays is due to it being a III-SD, which is more sensitive than a III-V (Tykot personal communication 2012).

The pXRF data gathered from ceramic samples was converted using calibration software to produce numerical data on a suite of elements (Ba, Fe, Rb, Sr, Y, Zr, and Nb). The analyses were conducted at analytical settings different than those specified for the calibration software (40 kV, 10 uA, with a filter). The numeric data produced, however, are still valid for use in differentiating source groups, in particular because no other studies have been done with data to compare with. Of these elements the five trace elements (Rb, Sr, Y, Zr, and Nb) were selected for statistical analysis. Trace elements are of particular interest in chemical sourcing because clays from the same procurement zone
tend to be similar in their chemical composition (Bishop 1980; Bishop et al. 1986) and they do not seem to reflect significant weathering or substitution (Bishop 1982:298-299).

Since each sample was analyzed twice (inner and outer surfaces) the numerical elemental data for each sherd was averaged before performing statistical analysis. The elemental data were subjected to discriminant function analysis with SPSS 20 statistical software. This multivariate statistical technique presupposes the existence of a given number of known groups based on some criterion, attempts to find ways on the basis of an independent criterion and is concerned with allocation of individual items to the groups in which they belong most appropriately (Shennan 1997). The independent criteria, in this case, the trace elements, are used as discriminating variables to predict the membership of each sample. The dependent criterion, in this case valley provenience, is the object of classification.

Statistical Analysis. The calibrated data on trace elements (Rb, Sr, Y, Zr, and Nb) from pXRF assays is reported in Appendix A:Table 1. Predicted group membership from discriminant function analysis is also displayed in variable Predicted Group Membership. For discriminant function analysis each sample was given a provenience value according to the valley it was found in (variable USULUTAN). Usulután types (Gualpopa polychrome, Izalco, Usulután special cream, and Chilanga) and Carolina Black were left blank as these were thought to be possible imports from outside the valley, namely from Copán.

In this study the given number of known groups was based on the sample’s valley provenience (LMV=1, NV=2, CV=3) no group was assigned to samples belonging to the Usulután tradition (Izalco, Chilanga, Usulután-Special Cream, Copador, and Carolina
Black), the independent criterion used to group the samples were the five trace elements. This initial statistical exercise showed that strontium, niobium, and yttrium were the most important elements in predicting group membership. The results also suggest that the vast majority of sample group membership correspond with sample provenience (see Table 1). Of note are the predicted group membership of samples (41-Q-52-Q) analyzed by the Penn Museum’s pXRF instrument, predicted membership was attributed to the Cacaulapa Valley despite all coming from the Quiriguá type collection. If we ignore this Quiriguá subset of data, a scatter plot of discriminant function show samples from the CV forming a distinct group, samples from the LMV and NV forming another group, with a third group being formed by a subset of NV samples (Figure 4.1).

Interestingly Naco and Cacaulapa Tipon type samples have, with only one exception, predicted group memberships for their valleys of provenience (Figure 4.2). This contrasts with previous conclusions (see Urban 1993) predicting that Tipon types found in Naco were likely Lower Motagua imports. Furthermore the graph suggests that Tipon sherds in the NV were likely produced from a secondary clay source (see discussion below).
Figure 4.1 Scatter plot of canonical discriminant function scores. Markers set by variable USULUTAN
Figure 4.2 Scatter plot of canonical discriminant function scores showing distribution of Tipon type sherds with other samples. Markers set by valley provenience.
If the samples analyzed with the Penn Museum’s pXRF are ignored most of the samples (87.2 percent, n=190) grouped with their valley of provenience, with few exceptions. This included the Usulután types, of which only one sample from the CV grouped in another valley (LMV). The visualization of discriminant function scores shows ceramic samples from each valley grouping with other samples of the same valley provenience. This is especially true of examples from the Cacaulapa and Lower Motagua Valleys. The Naco Valley is different, a subset of NV samples group closely to the LMV, while another groups by itself.

A number of inferences can be drawn from these results. First these results suggest that the samples were manufactured in the valley of their deposition, with perhaps a few exceptions. Most of the samples that group outside of their valley of depositions group as determined by discriminant analysis are from the NV and these samples group with the LMV. At first glance this may suggest that ceramics are being traded from one valley into the other. However, it may be a function of the very similar depositional histories of the two valleys. The overlap seen in the scatter plot does not indicate that any particular pottery type or class from the NV or LMV is grouping with a non-local valley, rather this overlap represents a breadth both utilitarian and fine wares with no tendency towards one or the other. Both the LMV and the west side of the NV (everything east of the Chamelecón River) have volcanic soils derived from the Sierra de Omoa Mountains (Wells personal communication 2012). Given this similar depositional history it is not unlikely that ceramics from these neighboring valleys should have similar chemical signatures. Naco Valley sherds that form a separate group may be derived from a secondary clay source or sources and show chemically different signatures as their
parent material is derived from sedimentary soils on the east side of the Chamelecón. Of particular interest is that all Usulután types, including Copador group with their valley of archaeological provenience. If these were indeed imports from the Copán area or another area one would expect them to group together but they group centrally to their valley of deposition. This suggests that both the LMV and the CV locally produced Usulután type wares in the Classic Period. No Usulután samples from the NV were sampled in this study. Tipon wares deposited in the CV (1), LMV (14) and NV (9) with one exception (see above) also group with their valley of deposition. This suggests that production of Tipon type pottery was also produced of clays in their valley of archaeological provenience.

Discriminant analysis of the trace elemental data on ceramics shows that three elements are most important in the two functions used to discriminate groups, Nb, Y, and Sr. Function one is responsible for 90.9 percent of the variance and Nb and Y are responsible for this function. Strontium is the most important in function two and this function explains 9.1 percent of the variance. Further scrutinization of these data was conducted by creating a 3-D scatter plot of the samples setting markers by valley and using Sr, Y, and Nb as the X, Y, and Z-axes respectively. The 3-D scatter plot can be rotated to determine which element is most important in determining each valley group. Below the results are graphically displayed by simple X-Y scatter plots of elemental data comparing two elements at a time (Figures 4.3-4.5). For each valley one element was determined to be most important in differentiating it from the other two. Treated as a group the Cacaulapa Valley sherds can be differentiated from the other two in a number of ways. Figure 4.3 shows that treated as a group CV sherds have lower Y and Nb values
than the LMV and the NV. Distribution of CV material is similar in Figures 4.4 and 4.5. As previously discussed it is likely that many of the NV samples were made from materials similar to those of the LMV but that a subset of these sample come from materials from the east side of the Chamelecón River. This subset differentiates from the LMV group in Sr concentrations (Figures 4.4, 4.5).

Figure 4.3 Scatter plot showing concentrations of Y and Nb. Markers set by valley.
Figure 4.4 Scatter plot showing concentrations of Sr and Nb. Markers set by valley.
Figure 4.5 Scatter plot showing concentrations of Sr and Y. Markers set by valley.

**Additional data collection: El Coyote Ceramics.** An additional set of data was collected on the sherds from El Coyote (83) with the third machine (see above) using settings of 40kv, 10µ with no vacuum and a filter for 120 seconds. This round of assays provided interesting results for testing the validity of the machine by comparing results from the two settings. The results of this round of assays, which produce calibrated values in ppm, are reported in Appendix A: Table I.2.

A Pearson’s correlation matrix was created for the trace elemental data from both rounds of analysis. To perform this analysis each column of elemental data was given a
number corresponding to the analysis that produced it. All data gathered with the 40kV, 10µA and the filter were given a “1” and data gathered at 40kV, 1.5µA with no filter was given a “2.”

The table below shows that the results of both analyses while different numerically are statistically correlated. This suggests that while different settings may produce different numerical data these datasets are valid and comparable by implementing an offset treatment.

Table 4.1. Results of Pearson’s correlation on pXRF data taken at two different analytical settings.

<table>
<thead>
<tr>
<th>Correlations</th>
<th>Rb1 Pearson Correlation</th>
<th>Rb2 Pearson Correlation</th>
<th>Sr1 Pearson Correlation</th>
<th>Sr2 Pearson Correlation</th>
<th>Y1 Pearson Correlation</th>
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<td></td>
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<td>Rb2</td>
<td>Sr1</td>
<td>Sr2</td>
<td>Y1</td>
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<td>-.355</td>
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<td>.400</td>
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<td>Sig. (2-tailed)</td>
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<td>.000</td>
<td>.001</td>
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<td>N</td>
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<tr>
<td>Rb2 Pearson Correlation</td>
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<td>-.255</td>
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<tr>
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<td>-.353</td>
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<td>Sig. (2-tailed)</td>
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<td>Sr2 Pearson Correlation</td>
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<tr>
<td>Y1 Pearson Correlation</td>
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**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

**Prospection Experiments: Plaster**

*Research Design.* The use of pXRF instruments for archaeological field characterization of chemical residues is growing. However, the technology is of limited use where it is desirable to isolate (for example through chemical extraction) the
anthropogenic inputs from the mineralogical components (McCormick et al. 2011). Seven soil and seven plaster samples were taken from the surface of a room in structure 127, of the main plaza at El Coyote with a stainless steel scoop and knife and stored in sterilized Whirlpack bags (McCormick et al. 2011).

The pXRF examination of plaster was performed at the University of South Florida Laboratory for Archaeological Science. Ramunas Jakimavicius (an undergraduate honors student at USF) and I conducted the sample preparation and pXRF assays under the direction of Dr. Robert Tykot. The samples were provided by Dr. Christian Wells and were collected from the same plaza El Coyote as part of the CVP (E. C. Wells, personal communication 2012). These samples are currently housed at the University of South Florida Mesoamerican Archaeology Laboratory.

For the pXRF analyses, we first performed non-destructive analysis on the surface of seven plaster samples in two quantitatively different areas, those with macroscopically visible residues or “dark” and those without or “white” (McCormick et al. 2011). Some of these plaster samples did not have sufficient “white” surfaces and so a rotary drill was used to clean a small portion of “dark” surface so as to have a clean analyzable surface. Second, each specimen was vertically split using a rotary saw in half in order to facilitate testing of homogenized powder samples. A rotary drill was then used to grind down a portion of the ballast and the plaster surface for separate testing. Inclusions within the ballast were removed and not included in the powder samples. The powder samples were mesh-filtered to so that only fine particles of powder remained for analysis. This filtering process is necessary because air gaps between particles could potentially interfere with data collection. With both material treatments, we analyzed the samples with both a filter
used for trace elemental analysis and without a filter but with a vacuum (for major element analysis) (McCormick et al. 2011).

The data gathered on plaster samples from El Coyote all underwent assays of 180 seconds. The settings for the surface analyses (non-destructive) were 12kV, 30µA with a vacuum and no filter (setting I). This setting was specifically used to gather data on elements indicative of human activity, P, K, Ca, and Fe. Sodium (Na) and lower Z elements are not testable with this instrument. At this point work is still ongoing for quantitative calibration for these settings, using recent testing of Smithsonian and other standards. The powder samples (semi-destructive) settings were 40kV, 10µA with no vacuum and a filter (hereafter setting II). Solid samples (both “white” and dark” were placed upside-down on top of the X-ray beam. Powder samples were placed in a plastic hexagonal dish for analysis that was regularly cleaned to avoid cross contamination. Although the dish was penetrated by X-rays its material does not interfere with the elemental results (Tykot personal communication 2010). The data collected with the filter settings were calibrated using software against known standards used in multiple laboratories, including the Missouri University Research Reactor and the Smithsonian Institution. The calibrated software is based on silicate-based standards not calcium based ones as there were no calcium based standard calibrations available for pXRF at this time. The numeric values reported here are valid but may not be comparable with those gathered at other labs (Tykot 2012, personal communication).
Figure 4.6. El Coyote Main Plaza (reproduced from McCormick et al. 2011).
**Results.** The results of assays conducted at 40kV, 10μA with no vacuum and a filter (setting II) are shown in Table 4.2. Preliminary observation of these data show that most of the samples have fairly similar values of the elements reported. However, sample 25AA-33 (hereafter P-33) stands out with high values of Ba, Mn, Fe, and Sr. Prior to pXRF analysis it was also noted visually that this sample looked different from the rest. This suggests that this plaster is different, and perhaps represents inclusion of ankerite minerals in the otherwise dolomitic limestone. Ankerite is closely related to dolomite but differs from it having magnesium replaced by varying amounts of iron and manganese. While its trace element concentrations for Rb, Y, and Zr values are in step with the other samples its Sr value is much higher. As discussed above trace elements are those most commonly used in sourcing and so one may interpret the high Sr values as indicative of a separate source for sample P-33. However, this may be a function of a different manufacturing process used in the creation of sample P-33.

Data gathered with setting II were not calibrated into numerical data as there is currently no good calibration formula for the instrumental settings for this material (plaster). Nevertheless the peak graphs produced in the pXRF software do provide useful quantitative (even if not numerically accurate) results. Quantitative analysis of the vacuum enabled pXRF data on the plaster samples agrees with those conducted at setting II. Comparing peaks of the samples allows visual assessment of the different plaster samples. Comparison of “white” vs. “dark” surfaces shows that clean samples give higher readings of Ca and lower readings of Fe. A negative relationship between these elements exists: as peaks of Ca go up Fe peaks decrease. Since Ca is a key component of limestone
this is not surprising, assays of cleaned surfaces will be more representative of the raw materials used in creating the plaster as opposed to its anthropogenic inputs.

Iron is also an element of interest, as “dark” surfaces show higher readings than on white surfaces. Again this is likely a function of the anthropogenic inputs on “dark” surfaces. Here sample P-33 stands out with higher Fe concentrations than any other sample. A comparison of P-33 also shows a sharp decrease in the amount of Mn (along with Fe) from the “dark” vs. the “white” sample. This is difficult to interpret but suggests that here Fe and Mn peaks are somehow associated with the visible residue on the surface.

Both the numerical elemental data from setting II suggests that sample P-33 is different from the other 6 plaster samples. However, where this difference comes from is difficult to ascertain. It is possible that it comes from different parent material than do the other samples, but it is also possible it represents a difference in the manufacturing process. The high levels of Fe in “dark” surface samples, in comparison to “white” surface samples, suggest iron is a post-production input. It is unclear whether this input is a product of human activity or natural post abandonment deposition. The relationship between Mn and Fe is positively correlated in all the samples and is found in higher concentrations in “dark” surface samples than it is in “white” surface or powdered samples.
Comparison of Plaster pXRF and Soil ICP results

The original impetus of the pXRF analyses conducted on plaster samples from El Coyote was to test the appropriateness of using pXRF in investigating human activity areas. As previously discussed one of the methods used in studying such areas is ICP-
MS. This section presents the results of a multi-elemental comparison between a Bruker III-V pXRF and a Perkin Elmer Elan-DRC-II ICP-MS on soil and plaster (see Appendix II) and soil samples from the same deposits at El Coyote reported in a conference paper at SAA meeting in 2011 (McCormick et al. 2011). A multivariate quantitative assessment of the data contextualizes the prospects of pXRF technology for activity area analysis in archaeological research. Before presenting the results I will first give a synopsis of the analytical procedure performed on the soil samples.

Soils

**Research Design.** The preparation of the soil samples (7) from El Coyote for ICP-MS analysis followed methods described in Wells (2004), a 2.00 g portion was taken from each sample, pulverized with a Coors porcelain mortar, mixed with 20 ml of dilute 0.60-molar hydrochloric acid (trace metal grade) with 0.16-molar nitric acid in a polyethylene scintillation vial, and shaken vigorously on an electronic shaker at 220 rpm for 30 minutes. For each sample, the solution was filtered using Whatman ashless filter paper and decanted into clean polyethylene vials. The extracts were then diluted with ultrapure deionized water to bring the concentrations of the elements of interest into the optimal measurement range of the instrument.

All samples were analyzed using a Perkin Elmer Elan II DRC quadrupole inductively coupled plasma-mass spectrometer at the Center for Geochemical Analysis at the University of South Florida. For calibration, known solution standards containing the elements of interest in concentrations bracketing the expected concentrations of the sample were run during the analysis. By running several standards of different concentrations, calibration “curves” were generated equilibrating instrument response
with known concentration. The unknown data were then plotted on these curves and the amount of each element of interest was calculated. The calibrated concentrations of 21 elements were determined. The results were reported in parts per million of the element and subsequently converted to mg of element per kg of soil by multiplying the ppm measurement by the dry weight of each sample.

The data were converted from ppm to base-10 logarithms for comparability, since natural abundances of elements tend not to have normal distributions but to be positively skewed and log-normally distributed. Since the objective is to compare the results of two different instruments used to analyze two different geological materials, each log-10 elemental concentration was divided by the log-10 of Fe (the most abundant element in each sample matrix, where variation is mineralogical and not anthropogenic). This allows qualitative comparison of the data; this does not allow statistical comparison. In this study, again for purposes of comparability, comments are confined to Ba, Ti, Mn, and Sr.

**Comparison of results of geochemical investigation on plaster and soils from El Coyote.** The results of the geochemical analyses conducted on plaster (pXRF) and soil (ICP-OES/MS) samples from the backside of structure 127 at El Coyote were conducted using two different instruments. When observing the results it is important to remember that the two methods are inherently different in a number of ways. First pXRF analyses are conducted on the sample as a whole whereas ICP-MS analyses are conducted on liquid extracted from samples. The extraction methods (above) are used to isolate anthropogenic inputs in the sample. Secondly both non-destructive and semi-destructive pXRF assays were done on the plaster samples. The non-destructive assays gather data only on an area the surface of the sample, whereas the semi-destructive powdered
samples represent homogenized pieces of the sample. Third by virtue of the difference in instrumentation these methods analyze for different elements and so only a subset of elemental data gathered by each method is available for comparison.

Both instruments gathered data on Ba, Ti, Mn, and Sr. Comparison of the elemental data in ppm is displayed as a boxplot (Figure 4.7). This boxplot compares the ranges and median values of the data. It can be observed that both Ba and Ti from the plaster samples are consistently higher in concentration than those of the soil samples. This is to be expected as pXRF data represent elemental concentrations of entire specimens (both diagenetic and anthropogenic), whereas ICP data represent concentrations of extracted ions (anthropogenic only). It can be observed that Mn and Sr

![Figure 4.7. Boxplot of averaged ppm concentrations on plaster samples analyzed with pXRF and soil samples analyzed with ICP-MS showing comparisons Ba, Ti, Mn, and Sr.](image-url)
are generally within the ranges of variation for both pXRF and ICP results. This is especially true of the pXRF assays conducted on solid samples (both “dark” and “white”). The powdered samples show a decrease in both. The Sr is most likely related to Ca in the plasters and soils, which both derive from dolomitic limestone substrate (McCormick et al. 2011). The slightly higher concentrations of Mn in ICP data (compared to pXRF) data may be due to the extraction process. However, concentrations of Mn in the “dark” surface plaster samples and soil are almost equal. This is not surprising as the analyzed residue of the “dark” samples is most likely soil.

McCormick and colleagues (2011) also interpolated the data using Kriging with a semi-variogram model and plotted them spatially with the software program Surfer. Kriging assumes that areas close together are more similar than areas that are further apart, using a variogram model to characterize the degree of spatial correlation (Wells 2010; Rothenberg 2011). The resulting images represent visual probability plots of each variable as it changes spatially. The image below compares Ba and Ti distributions of the ICP soil data with dirty surface plaster samples. It can be observed that the pXRF data yield visually different patterns than the ICP data. As noted above, this is explained by the nature of the different analyses, pXRF being representative of entire specimens (diagenetic and anthropogenic) and ICP being representative of extracted ions (anthropogenic only). Isolation and characterization of the anthropogenic contributions, here through acid extraction, a different spatial pattern is revealed when compared to the pXRF method which considers the entire mineralogy of the samples.
Figure 4.8. Kriged variogram comparing Ba and Ti distributions of pXRF data from dirty plaster samples and ICP-MS data from soils.
The results presented in the preceding chapter elucidate both the strengths and the limitations of pXRF as an analytical tool in compositional studies on southeast Mesoamerican earthen materials.

**To What Extent can pXRF be used in Provenance Studies?**

*Can pXRF (vs. INAA) be used to create reference groups?* The discriminant function analysis on trace elemental data shows that pXRF can be used to identify reference groups. The tight grouping of samples with their valley of archaeological provenience suggests that data produced by pXRF is useful for creating geochemical source groups with ceramics from southeast Mesoamerica. Discriminant function analysis was also useful identifying specific elements useful in differentiating one reference group from another. As discussed above function one was important in differentiating samples from the Lower Motagua Valley and Naco Valley from those from the Cacaulapa Valley. Function two was important in differentiating a secondary procurement source for a subset of sherds found in the NV from those chemically similar to those found in the LMV. While a second clay source is indicated by the values distribution of this subset of NV sherds, where this clay source is geographically located is difficult to say. I suggest that these may be derived from Naco Valley clays on the east side of the Chamelecón River, whose chemical signature differs from those on the west side due to their different geological histories. It is also plausible that these sherds represent imported wares,
although the ceramic typology would suggest otherwise. It is my opinion that these samples are indeed of local manufacture, as the samples do not represent ceramic types that have high prevalence in neighboring valleys except the LMV. It must be noted here that data produced from the Penn Museum’s pXRF did not conform to the trend mentioned above. This may be due to inter instrument variation or a lack of instrumental calibration of the Penn Museum’s machine as it was not tested against known standards as were the two University of South Florida instruments.

Previous studies have shown that regular and portable XRF machines can produce data comparable to INAA data to identify source groups on southeast Mesoamerican obsidian (e.g., Fowler et al. 1989; Moholy 1999; Moholy et al. 1984; Rice et al. 1985; Stross et al. 1983; Smith et al. 2007). Similarly, in other parts of the world, recent studies have used pXRF to produce source groups and compared them with those produced by INAA analyses (Forster et al. 2011; Goren et al. 2011; Speakman et al. 2011). These studies show the ability of pXRF generated data to distinguish source groups comparable to those created using INAA data, which has long been the preferred method.

**Can pXRF (vs. INAA) be used to distinguish imports?** It is inconclusive whether or not pXRF can be used to distinguish imported ceramics from the material gathered in this study. The sample did not contain any “known” imports. It is also important to note that this study is experimental and reports the entire corpus of ceramic samples from southeast Mesoamerica analyzed by pXRF instrumentation. Prior to this study there were no site or valley reference groups to compare results with. This is especially important when looking into issues of trade because trade presumed trade items would need to be attributable to some known profile.
The ceramic types which would be presumed as trade items in this study include Usulután/Copador, probably coming from Copán to all three valleys and Tipon types, probably coming from Quiriguá to the Naco and Cacaulapa Valleys. The elemental data suggests that this is certainly not the case for most Tipon ceramics found outside of the LMV. The lone Tipon sample from Coyote fits squarely within its valley group. Eight of the nine Tipon samples from La Sierra group with the Naco Valley group and all eight are probably made of clays derived from the east side of the Chamelecón River as evidenced by their separation in distribution by discriminant function scores. A second possibility is that the eight Tipon samples that group apart represent trade items from another valley possibly Copán. Extensive studies have been done on Copán ceramic typologies (see Viel 1993; Willey et al. 1994; Bill 1997) and these note a similarity between Copán’s Surlo type and Quiriguá’s Tipon type. It is quite possible that the NV Tipon sherds are in fact from Copán (Surlo) and this is the reason for their not grouping with samples made from Sierra Omoa derived substrate.

One Tipon sherd from La Sierra groups squarely with the LMV group, suggesting this is indeed an import. But here it is important to remember that the raw materials used for ceramic production in the LMV and the west side of the NV have similar depositional histories, both are essentially derived from the parent rock (volcanic), the Sierra de Omoa Mountains. The raw materials on the east side of the valley by comparison are sedimentary and so different chemical signatures for ceramics produced from this material would be expected.

To date the material from the three valleys discussed are the only samples to have been analyzed by pXRF in southeast Mesoamerica. There are no databases of directly
comparable data (pXRF produced) from Copán or El Salvador, which have been proposed by others to be centers of Usulután and Copador ceramic production for the southeast (e.g., see Demarest and Sharer 1982; Bishop et al. 1986; Neff et al. 1999). It may very well be that armed with a reference group from either Copán or El Salvador (or both) analysis of the data would show that the Usulután samples analyzed in this study are indeed coming from outside the valleys of their deposition. As discussed above this may also be the case for eight of the nine NV Tipon type samples. However, the clustering of the Usulután sherds discussed in this study do not support this possibility, as both the CV and LMV Usulután samples group centrally with other samples of their valley of deposition.

Overall the results suggest that each valley was manufacturing foreign style ceramics with local materials for local distribution. This certainly does not mean that these valleys did not interact with one another. In fact the similarity in ceramic typologies suggests that these valleys shared ideological ties with each other and southeast Mesoamerica writ large. This is especially evidenced by Usulután ceramics in both the LMV and CV as this style is distributed throughout the region. Usulután ceramics were also reported from the NV but none were available for analysis at the time of this study. Presence of locally made Tipon style ceramics indicates the NVs ties with the LMV. This interaction between valleys is not only evidenced by the ceramic record but also by the large amounts of Ixtepeque obsidian found which indicates participation in the southeast Mesoamerican obsidian trade, thought to be largely controlled by Copán.
To What Extent can pXRF be used in Prospection Studies?

Can pXRF (vs. ICP-OES/MS) be used to identify activity areas on plaster surfaces? The pXRF data gathered on plaster samples shows that pXRF can be used to characterize plaster surfaces with both visible residues and those without as well as powdered samples of the plaster surfaces and their ballasts. It can be inferred that the “dark” plaster surfaces are more representative of human activity. A number of studies have found that levels of Fe (Barba and Denise 1981; Fernandez et al. 2002; Wells 2003; Middleton 1996, 2004) and Mn (Fernandez et al. 2002; Wells 2003; Middleton 1996, 2004) are useful in identifying human activity. However, the use of pXRF in studies of human activity areas on plaster is limited as the combination of settings and calibration software used in this study are not able to produce numerical data on other key elements of interest (i.e., P, Ca, K, Mg) in patterning human activity (see Wells et al. 2007). As mentioned in the previous chapter an important concern is the nature of pXRF analyses, which gathers data on both the diagenetic and anthropogenic inputs of the sample. This differs from other methods used in prospection that use extraction processes to isolate anthropogenic inputs for analysis (i.e., ICP-OES/MS).

Unfortunately at the time of this study we lacked calibration software to produce numeric data on elements lower than Mg, limiting the utility of Bruker Tracer III-V pXRF in prospection studies. The fact that the non-destructive methods used in this study do not isolate anthropogenic inputs is also a concern. Essentially the nature of the instrument, if used on untreated, non-homogenized samples, does not allow for the same type of investigation as other geochemical (extraction) methods.
Can pXRF (vs. ICP-OES/MS) be used to identify activity areas on soil surfaces?

It is unclear if pXRF can be used to identify activity areas on soil surfaces. However, the recently accepted manuscript by Gauss and colleagues (2013) using pXRF to identify ancient activity areas shows promise. While it is not surprising more established methods of analysis (i.e. ICP-MS, atomic absorption spectroscopy) are preferred in analyzing soils for anthropogenic inputs, pXRF is beginning to be tested in this avenue (see Abrahams et al. 2010; Johnson 2012; Gauss et al. 2012). As this study did not incorporate soil samples analyzed with pXRF it is difficult to determine the Bruker Tracer III-V instrument utility here.
Chapter 6: Conclusion

This study has shown the applicability of pXRF in geochemical compositional studies in southeast Mesoamerica. Others have shown its ability to accurately source obsidian in this area, while still others have shown its use to chemically attribute ceramics to particular geographic regions in other parts of the world. Previous studies have shown that human activity patterns can be examined using geochemical methods, and this study shows that pXRF may be able to produce usable results for archaeological prospection, but that its applicability is limited.

The reason for using pXRF instrumentation is its ability to collect simultaneous multi-elemental data on archaeological material, in a rapid, cost-effective, and non-destructive manner. These benefits are of key importance to the archaeologist, who operates under the desire to cause as little destruction as possible to the material record. Non-destructive analysis is ideal in any scientific endeavor, as it leaves the sample undamaged so that the study can be replicated. It is also important when dealing with sensitive material as the owners, whether they are museums, private collectors, or nation-states, are often opposed to sending material to off-site laboratories for analysis, let alone those that employ destructive methods.

pXRF is, by no means, a magic bullet; it cannot answer all archaeological questions. The nature of being a non-destructive instrument means that it is a surface analyzer. It only penetrates a millimeter or less, depending on the material, which limits
the depth of the sample being assayed. This is especially important when examining the
earthen materials analyzed in this thesis, ceramics and plaster. Assays of ceramics gather
data on the surface and may not be gathering data on the entirety of the paste. Although
this may not be of concern in this study, as slips (when applied) were made of the same
clay as the paste (Sharer, personal communication 2012), this could pose an issue when
dealing with glazed ceramics or manufacturing processes that used a separate clay source
for the slip.

The results presented in Chapter 4 have shown that pXRF can be used to create
source groups on ceramics from southeast Mesoamerica. Through statistical analysis, it is
shown that ceramic samples from different valleys grouped for the most part with
samples of the same archaeological provenience. I have also shown that this statistical
analysis grouped ceramics, whose typology may suggest importation, also in their valley
of deposition. While this may be a product of the sample size and absence of samples
from the possible origin(s) of these samples, the statistical analysis suggests that potters
in each valley may have produced their own local versions of foreign-style ceramics (see
Neff et al. 1999).

Analysis of the elemental data gathered on plaster show a substantial difference in
elemental levels based on the preparation method. This indicates that, while pXRF data
may be able to show that activities took place in the spot analyzed (i.e., the cleaned
surfaces differed from those with observable residues), determining the specific nature or
type of activity is not so straightforward.

Both archaeological provenance and prospection have been investigated through a
number of destructive methods. These methods are different in nature from pXRF. In
many provenance studies a portion of the sample is taken, homogenized, and destroyed in
the process of analysis. Although this may gather data more representative of the entire
sample matrix, it does not allow for repeated analysis and it also destroys a portion of the
specimen in the process. Prospection studies take a portion of the sample and isolate the
anthropogenic inputs using an extraction method, usually involving some type of acid.
All these methods, while gathering more representative data, cannot be exactly replicated
as the sample is destroyed in the analytical process. Moreover, the work must generally
be completed in a laboratory and not on-site (but see Terry et al. 2000).

This study is largely experimental in nature, designed to explore the feasibility of
using pXRF in two separate lines of inquiry on material from southeast Mesoamerica.
The results of this study are promising. First, I have shown the ability of pXRF to
distinguish source groups with Classic Period ceramics. Second, I have shown that pXRF
can be used to locate activity patterns on plaster surfaces. Both of these findings have
implications for future research in Mesoamerica and archaeology at large. Whenever a
new technology becomes available to archaeology, its abilities and limitations must be
tested. Logically, these technologies will first be employed using methodologies and
research designs based on previous studies seeking to investigate the similar questions.
Portable XRF represents a new kind of instrument, one that is portable and non-
destructive but with the calibration software currently available is limited both in its
ability to conduct bulk analysis and accuracy in gathering elemental concentrations.
pXRF has the advantage of flexibility in that settings can be changed and filters can be
applied to gather more accurate data on chemical elements of interest depending on the
question(s) being asked and the material(s) being analyzed. Software has been developed
to produce accurate and precise concentrations for trace elements used in this study, but with different analytical settings.

In provenance studies, the development of calibration software based on ceramic standards is important. Instruments should be shown to give similar results on the same material so that datasets gathered by different analysts with different instruments can be compared. Since pXRF does not gather information in the same way as INAA or ICP-MS, results will differ. This does not mean that they are ultimately incompatible. As others have shown with obsidian, if the same geological sources are analyzed, pXRF can readily differentiate one group from another, thus results from different instruments can be compared. The same is true of pXRF’s use in prospection studies. While this is admittedly more difficult to ascertain presently, as there is a paucity of studies that have been performed in this line of inquiry with pXRF instrumentation, it can still be developed. Key in developing methods for the use of pXRF for prospection is conducting ethnoarchaeological studies on human activity and attributing them to elements analyzable by pXRF instrumentation (Wells et al. 2007).

It is important for the analyst to know their instrument. Not all pXRFs are the same; each make and model seems to have its own relative strengths and limitations. One may be better for analyzing one material, and another instrument may be more adept at analyzing another. It is important to know the applicability of not only the machine being used but also the proper settings and filter(s) (if applicable) to apply to obtain the most usable results for the question(s) being asked.

Portable X-ray fluorescence spectrometry may not replace more established destructive methods of analysis but, for rapid, non-destructive, simultaneous multi-
elemental gathering of data, it presently has no equal. In recent years, pXRF has enjoyed increased popularity in a number of disciplines including archaeology as an analytical method, and will undoubtedly continue to do so.
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Appendix I
Calibrated Elemental Data on Southeast Mesoamerican Ceramics
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Appendix II
ICP-MS Elemental Data on Soils from El Coyote
Table A.II.1 Calibrated elemental data from ICP-MS analysis done on soil samples from El Coyote

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