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Characterization of the Deterioration of Low-Fired Ceramics
in Varying Burial Environments

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Arts
in Conservation of Archaeological and Ethnographic Materials

by

Elizabeth Johnson Drolet

2012

ABSTRACT OF THE THESIS

Characterization of the Deterioration of Low-Fired Ceramics in Varying Burial Environments

by

Elizabeth Johnson Drolet

Master of Arts in Conservation of Archaeological and Ethnographic Materials

University of California, Los Angeles, 2012

Professor Ioanna Kakoulli, Chair

This paper investigates the effects of heavy shell deposits on the condition of low-fired ceramics using the Late Archaic fiber-tempered assemblage from St. Catherines Island, Georgia. Through combined non-destructive analytical techniques, including variable pressure scanning electron microscopy (VPSEM) and portable X-ray fluorescence spectroscopy (pXRF), the structural, chemical, and physical deterioration is examined. This study seeks to determine the efficacy and limitations of non-destructive analysis in the investigation of deterioration processes. Limited destructive analysis using thin-section petrography is employed to complement the non-destructive testing. The condition of ceramics recovered from dense shell deposits is compared with those from shell-free areas of the site. The paper discusses the effect that the burial environment has on changes in preservation, as well as the consequences that these changes have on the excavation, storage, and analysis of these materials.

The thesis of Elizabeth Johnson Drolet is approved.

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CHAPTER I: INTRODUCTION

The deterioration of ceramics is an important, though often overlooked, issue in archaeological excavation and analysis. The inorganic constituents and the durability of these materials have led ceramics to be regarded as immune to common deterioration processes affecting other material types. Despite this, deterioration processes can affect the survival and stability of ceramics. With growing interest in the effects of weathering processes on ceramic artifacts, there have been recent studies of the chemical, physical, and mineralogical composition of ceramics, and the interaction that these materials can have with the burial environment. Research has typically focused on changes as they relate to results from provenience and dating studies. The goal of this study is to examine the variation in ceramic composition that results from burial and post-depositional processes in different soil environments, and the effect that these chemical and physical changes have on the overall preservation of ceramic sherds. As a case study, ceramics from the St. Catherines Island Shell Ring (9Li231), a Late Archaic site in the Southeastern United States, were selected for examination. The sherds at the site show disparate states of preservation, although they were excavated in close physical proximity. By comparing the resulting level of preservation with the chemical composition of the sherds and the properties of the surrounding soils, a better understanding of the deterioration processes of these materials can be reached. The impact of the resulting conditions on the excavation, analysis, and storage of the ceramic materials will be discussed.

STATEMENT OF THE PROBLEM

Ceramics are highly important for the understanding of the archaeological record; it is thus important to understand the post-depositional factors acting upon them in burial in order to implement excavation and storage strategies that will effectively ensure their preservation. Many

early Southeastern ceramics such as the ones examined in this study are found in conjunction with shell deposits. The burial conditions associated with these deposits – shell middens in particular – can strongly affect the preservation of archaeological materials buried within them. Understanding the deterioration processes taking place, and the resulting preservation of ceramics found within shell deposits is relevant for the archaeologist during recovery and processing, as well as the archaeological conservator or collections manager responsible for their long-term stability and storage.

DETERIORATION PROCESSES OF CERAMICS

The chemical and physical interactions of materials within the burial environment directly affect the condition of archaeological ceramics as recovered. The deterioration of ceramics is primarily caused by interaction of the sherds with the burial environment as the temperature, water content, and chemical composition of the burial environment shifts. This can happen through a number of different mechanisms involving diffusion and transfer processes, and can be chemical and/or structural in nature (Purdy and Clark 1987:213-15). Low-fired ceramics, typically fired at temperatures below 1000°C, are especially susceptible to these processes due to the incomplete vitrification of the clay body. Vitrification begins to occur around 800°C, as components of the ceramic begin to melt and fuse. Once complete, as in the case of highly fired ceramics such as porcelain, this material fills the pores. Low-fired ceramics retain high porosity because this process is absent or incomplete, and this porosity provides a pathway and surface area for the introduction of external materials into the ceramic body. The presence of voids from tempering materials and the formation of cracks can provide additional means of entry for moisture, especially where these voids are interconnected (Buys and Oakley 1996:10,18).

After deposition, ceramics are typically highly resistant to deterioration once they have come to equilibrium with the surrounding burial environment. Much like other inorganic materials, such as glass or stone, the surface layers of the ceramic are first affected by weathering processes. The outer layers and pores will be affected by the burial matrix, with the resulting alteration products forming a protective corrosion layer, and leaving the core of the sherd relatively undisturbed. Exceptions to this occur when significant shifts in the burial conditions change the equilibrium of the sherd with the surrounding environment, and alteration products are again formed as the reactive ions within the ceramic again interact with the soil. This applies to both the exterior and interior surfaces of the sherd, as well as to any break edges – which provide major pathways for the introduction of moisture and external materials. The broken edges are particularly susceptible to these processes, and are subject to increased weathering and loss as a result (Franklin and Vitali 1985:13; Purdy and Clark 1987:213-14). Common changes in the burial environment include temperature and moisture level variations. Freeze-thaw cycles are known to affect the preservation of low-fired fiber-tempered ceramics, resulting in the disruption of the burial environment and severe deterioration (Reid 1984). Similarly, wet and dry cycles can also have a negative impact on the preservation of ceramics, providing sufficient stress on the ceramic body to result in partial or complete loss of the ceramic object (Murphy, et al. 1981).

Exposure to water is one of the most common sources of weathering for buried ceramic materials and can lead to leaching, dissolution, and precipitation of components from within the ceramic structure and from external sources (Maritan and Mazzoli 2004:673; Purdy and Clark 1987:212). Deterioration typically occurs through either selective leaching or matrix dissolution (Purdy and Clark 1987:215). When selective leaching occurs, specific ions are removed from the surface of the ceramic, leaving behind a depleted layer that varies from the original composition of

the ceramic. This layer can at times be distinct enough to separate from the bulk composition of the ceramic, especially in the case of ceramics without slips, glazes, or otherwise discrete original surface layers. Matrix dissolution occurs when external factors weaken the structural composition of the ceramic to the extent that material is lost from the surface. Dissolution is a mechanism by which material is extracted from the ceramic body, changing the chemical composition and weakening the ceramic structure. In this type of deterioration a distinct surface layer will not be formed, but the outer surface of the material will be completely or partially lost (Purdy and Clark 1987:216-17). Precipitation is a mechanism whereby material is deposited by the movement of water into pores or voids within the ceramic structure. In some cases, the mineralogical components of a sherd can be altered, when minerals originally present decompose into secondary minerals. Rehydration of clay minerals can also occur in low-fired ceramics, particularly those manufactured at temperatures around 600°C (Buys and Oakley 1996:26; Maggetti 1982:129).

Significant changes to the mineralogical components as well as the chemical composition of the ceramic can have broad effects for analysis, affecting compositional and sourcing data (Buxeda I Garrigós, et al. 2001). Highly mobile species within the ceramic and burial environment can migrate, leaching either into or out of a ceramic body. Phosphates and calcite are commonly precipitated within the ceramic structure as a result of infiltration from water (Maritan and Mazzoli 2004:679). The calcium carbonate from shells is highly mobile, given the presence of acids and moisture in the burial environment. Calcium will not leach out in the presence of seawater, due to saturation of the salt-water solution, but when inundated with rainwater or groundwater leaching can occur. In the case of shell middens, high amounts of organic matter are sufficient to provide the organic acids necessary to leach calcium carbonate from shells (Stein 2008:74-76).

The deterioration mechanisms are closely related to the chemical nature of the burial environment, and particularly to the acidity or basicity (pH) and the reducing or oxidizing potential (eH) of the burial environment. These mechanisms are especially pronounced in particularly low and high pH ranges. In high pH ranges, especially above a pH of 10, matrix dissolution is the most prevalent deterioration mechanism, but in pH ranges below 4, the mechanisms are more complex and are typically a combination of matrix dissolution and selective leaching (Purdy and Clark 1987:219).

CHAPTER II: SITE DESCRIPTION

CULTURAL CONTEXT – LATE ARCHAIC SOUTHEAST

The first evidence of extensive occupation in coastal Georgia appears during the Late Archaic period, spanning from about 3000 to 1000 B.C. This is a time-period typically marked by increased hunter-gatherer populations and significant social and economic changes in the coastal Southeast. One indication of these changes is the first appearance of shell ring sites. These rings are composed of large deposits of shell in shapes ranging from round, C-shaped, to oval and U-shaped configurations. Shell rings are found along the coasts of Florida, South Carolina, Mississippi, and Georgia (Heide 2002; Schwadron 2010; Thompson 2007). This site type is specific to the coastal Southeast and occurs only during the Late Archaic and the subsequent Early Woodland period (1000 to 0 B.C.). The rings vary in total size and range from 50 to 250 meters across (Russo 2002:8).

The construction of these large-scale structures provides important indicators of changing social distinctions and increased sedentism, although the function and motivation for their construction is still highly debated. Explanations for the creation of shell rings have highlighted a variety of possibilities, including shell rings as ceremonial locations and feasting sites, settlements, water sources, and monumental structures (Marquardt 2010:258, 66; Russo 2004; Russo 2008; Steponaitis 1986). Tied to these social changes are dramatic technological developments, notably the first appearance of ceramics in North America. The earliest pottery is a coarse, fiber-tempered ware, which appears initially at approximately 2500 B.C. along the coast of the Southeastern United States, at the mouth of the Savannah River (Elliott and Sassaman 1995). Some have speculated that the close development of both shell rings and pottery technology is related to the increased exploitation of coastal resources during this period, with ceramics aiding in the collecting and processing of

shellfish. Others have suggested that ceramics functioned as a prestige item, and were used in ceremonial contexts, and the topic remains a subject of debate (Russo and Heide 2004; Sassaman 1993).

Fiber-tempered pottery and the use of baked clay items characterize the Late Archaic pottery tradition on the Georgia Coastal Plain. These ceramics, termed the St. Simons ceramic type on the Georgia coast, are low-fired and heavily tempered with organic fibers. This ceramic type is closely related to the Stallings series found further north in the Savannah River Basin and the Orange series found on the Florida coast. They are commonly manufactured with both sand and organic temper, but are typically referred to as 'fiber-tempered' by convention (Sassaman 2004:31). The ceramic typology is divided into the St. Simons I and St. Simons II periods, a division marked by the appearance of decorated ceramics (Thomas and Guerrero 2008:374). Baked clay items are small and typically amorphous balls of fired clay. The exact use of these objects is unclear, but they were potentially used for indirect heating purposes, such as in the roasting of food, and appear at many sites in conjunction with early ceramic technology. The use of both pottery and baked clay items at sites indicates some variation in the use of these items, and possibly shows a shift from indirect to direct cooking methods as baked clay items become less common with the increased use of ceramics (Russo 2002:35; Sassaman 1993:135). The use of ceramic technology directly over a fire for cooking purposes does not appear to become prevalent on the coast until late in this period, and it is not until about 1500 B.C. that ceramic technology is found widely throughout the interior of Georgia and the rest of the Southeast (Sassaman 1993:43,155-56).

SITE OVERVIEW

The St. Catherines Shell Ring (9Li231) is located on St. Catherines Island, a barrier island on

the coast of Georgia in the Southeastern United States (see Fig. 1). The earliest excavations at the site were conducted by the American Museum of Natural History in the 1970s, when several test pits were excavated, and Late Archaic ceramics were initially identified. Full scale remote sensing and excavation of the site began in 2006 in continued excavations by the American Museum of Natural History. The ring measures approximately 70 meters in diameter, with shells deposited in a nearly circular ring that surround a shell-free central plaza measuring approximately 34 meters across (see Fig. 2). The site was plowed heavily during historic use of the island, and as a result, the southern two-thirds of the ring are heavily damaged and no longer visible on the surface. The depth of the shell deposits varies around the ring, in part because of the plow damage, but in the undisturbed areas it reaches approximately one meter (Sanger and Thomas 2010:47,50). Radiocarbon dating of the site has indicated that the earliest occupation occurred in the Late Archaic period. The construction of the shell ring is preceded by the formation of small pits filled with shell dating to 2540-2290 cal B.C. and found underlying the ring itself. Construction of the ring appears to have taken place between 2230 and 2030 cal B.C. (Sanger and Thomas 2010:65). The ring is formed of dense shell deposits, composed primarily of oyster shells, but also containing significant quantities of clam, periwinkle and mussel shells. There are sections of both whole and crushed shell deposits, and the shells are interspersed with layers and pockets of dark soil. At the site, ceramics have been recovered both from the shell deposits and from contexts within the shell-free plaza. The ceramics at this site are typically open wide-mouthed vessels, with broad bases compared to the height of the vessel walls. There is a tremendous amount of variety in the manufacture of the ceramics, with both round and flat bases, and rounded, flattened, and thickened rims. These are typically coarse, thick walled vessels, heavily tempered with organic materials. The vessels were potentially used for cooking, serving or in the processing of food, although there is no evidence of direct use over a fire.

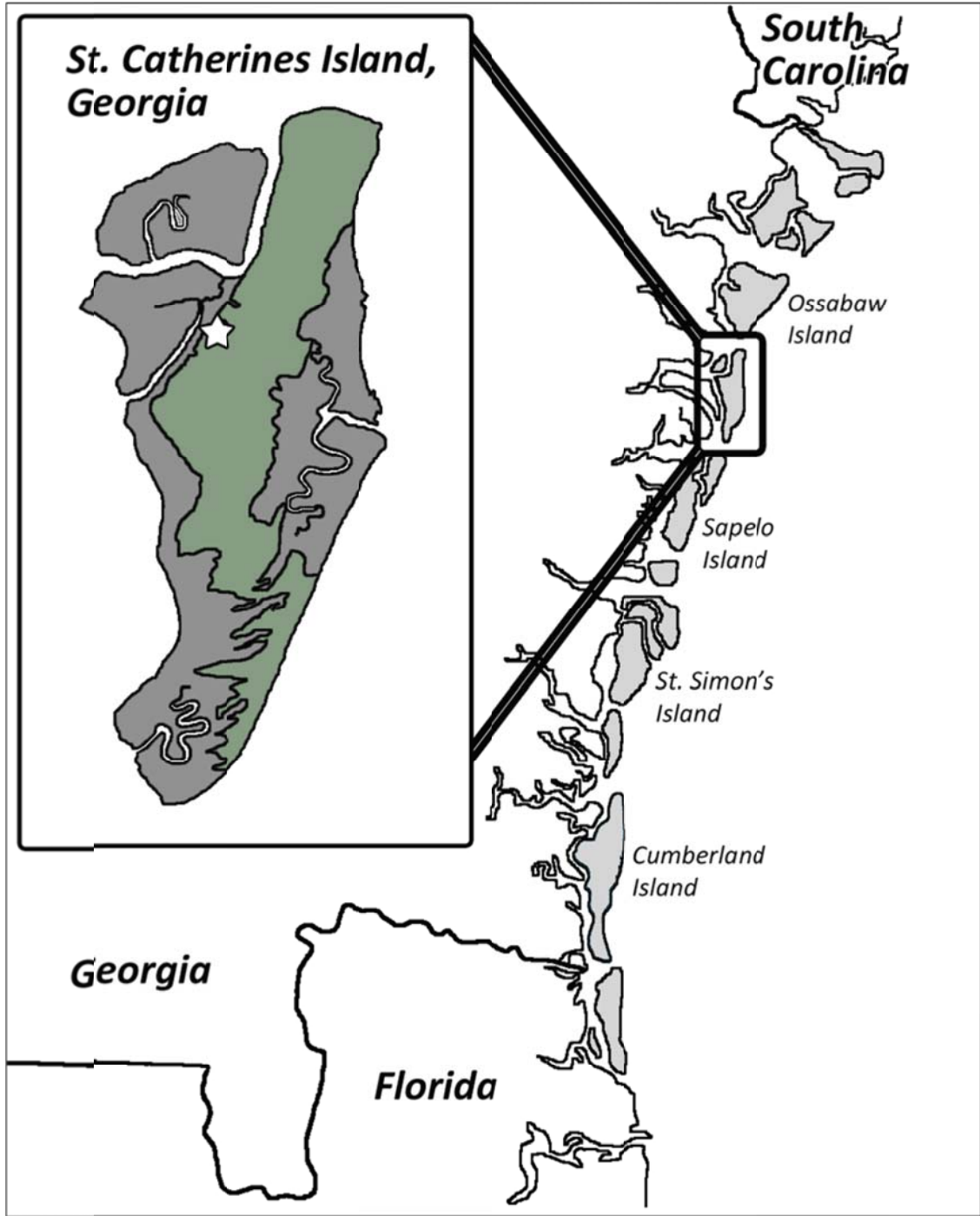


Figure 1: The location of St. Catherine Island, on the Georgia Coast. The star indicates the location of the St. Catherine's Shell Ring site on the western side of the island.

St. Catherines Shell Ring

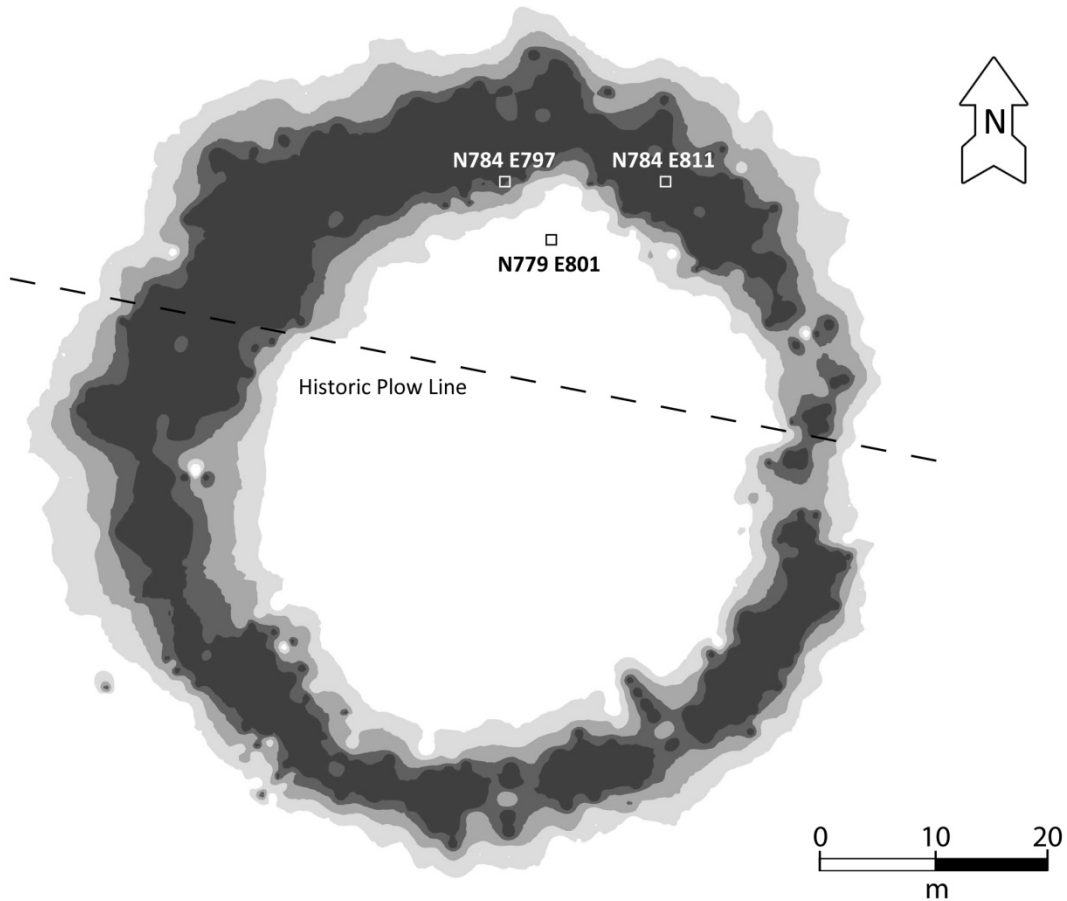


Figure 2: A map of the shell density in the St. Catherines Shell ring – dark areas indicate areas of heavy shell; light areas indicate areas of light shell. Image is adapted from a map created by Ginessa Mahar (AMNH).

Most likely, these vessels would have been used for indirect cooking purposes, with objects heated in a fire and placed into the vessel.

CRITERIA FOR UNIT SELECTION

Representative units were selected that are indicative of the general conditions of the site, and that contain more than thirty sizable sherds within the excavated levels. Units were selected from the dense shell deposits and from the shell-free interior plaza. Initially, two units were planned

for use in this study, one in the dense shell midden and one in the shell-free plaza. None of the excavated units in the dense shell had thirty sherds of sufficient size; instead, ceramics were taken from two separate dense shell units, N784 E811 and N784 E797. A single unit in the shell-free plaza, N779 E801, was selected for comparison (see Fig. 2). The units are all located within the northern, unplowed section of the ring, to minimize the likelihood of contamination or intrusion of more recent materials. Units with large intrusive features, as well as those with significant burning events were also avoided to eliminate these environments as variables that might affect the condition of the buried ceramics. Each unit selected also has paired soil samples for each level represented.

CRITERIA FOR SAMPLE SELECTION

Sixty sherds – thirty from each burial environment – were selected in two stages based on the minimum dimensions needed for their study and the representative nature and degree of deterioration. Sherds of approximately 2.5 cm in diameter and larger were selected to provide sufficient surface area for the planned analysis. Within the selected units, a survey was conducted to examine and classify each sherd according to major condition issues, and eliminate sherds smaller than 2.5 cm.

Based on this broad examination, the overall proportion of each deterioration type was tallied, and sherds were selected for analysis to reflect these values (see Appendix B). Rim fragments and decorated sherds were excluded, because of the destructive analysis needed in the course of the study. Only ceramics coming from levels in the dense shell deposit or completely shell-free areas were considered, in order to examine the most broadly dissimilar burial environments within the site.

CERAMIC DESCRIPTION

The ceramics recovered from this site are earthenware fired at low temperatures and prepared with organic fiber and sand temper (see Fig. 3). The large amount of aplastic quartz temper inclusions creates a porous ceramic paste typical of ceramics from this time-period. The sherds are generally partially reduced, with red and buff exteriors and dark cores caused by the incomplete oxidation of the ceramic during the firing process. The construction of the sherds is coarse and the composition of the paste is heterogeneous, indicating a lack of standardization in the production process.

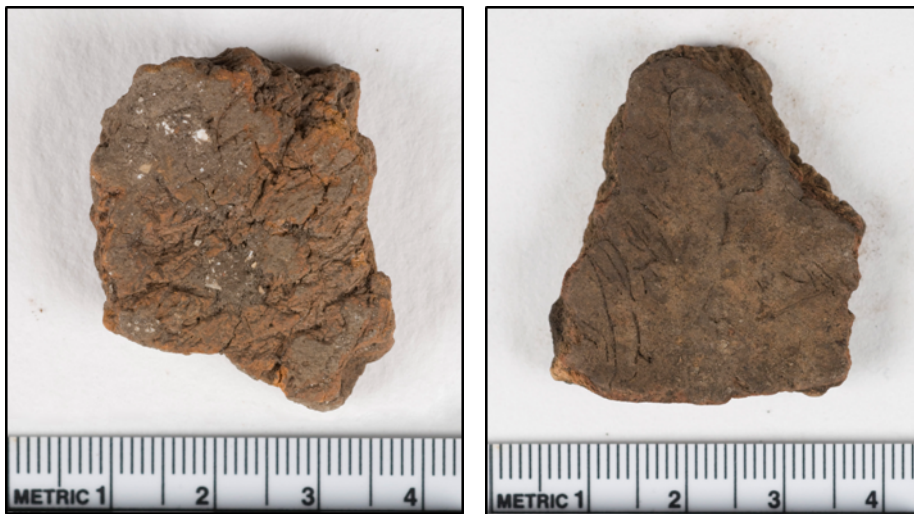


Figure 3: Examples of sherds used for analysis in this study, from the dense shell (at left) and the shell-free areas of the site (at right).

CHAPTER III: PREVIOUS RESEARCH AND LITERATURE

REVIEW

DETERIORATION OF CERAMICS

There is a limited amount of published research into the weathering and deterioration of archaeological ceramics. Much research has been done into the deterioration of other archaeological material types, including metals, glass and organic materials, especially that of bone. These studies typically focus on materials that are sensitive indicators of burial conditions and easily lost within the archaeological record. Ceramics have received little attention in this avenue of study, perhaps due to their overall durability, and many archaeological publications still treat them as being largely stable and resistant to significant deterioration (Freestone 2001). Within conservation literature, there is similarly a lack of interest in the topic of ceramic deterioration. Buys and Oakley (1996) give a general overview of chemical deterioration of ceramics and the effects of burial, but focus largely on physical and mechanical damage after excavation of ceramic materials. Sease (1992) includes a chart detailing the likelihood of deterioration for material types in specific burial environments, but this is one of few specific references to the issue as a whole. She indicates that alkaline environments will cause dissolution of the ceramic structure, but no further explanation of mechanisms or processes is given. Huisman's (2009) broad overview of the deterioration process of archaeological materials discusses each material type separately, including metal, bone, glass, and plant materials – but has no discussion of the degradation processes of ceramic materials.

Research into the composition and deterioration of ceramics has gone through several phases, with early research focused almost exclusively on the chemical composition of the ceramics. In the 1960s there was a great deal of interest in the topic, and many early publications resulted from excavators attempting to distinguish chemically between ceramic production areas (Catling, et al.

1963; Freeth 1967). These studies were typically concerned with variations in elemental composition as an indicator of production zone, and did not address the possibility of burial-induced changes in these compositions. Similar studies have continued since then, utilizing chemical information to characterize a range of temporal and geographic classes of ceramics in various parts of the world.

With the growth of behavioral archaeology in the 1980s, there was a corresponding shift in interest to the markers of weathering and use-wear in ceramics. While much of the research aimed to differentiate use-wear from other alterations, these attempts resulted in the first studies specifically or tangentially examining the ways in which the burial environment could potentially affect ceramic assemblages. Michael Schiffer and James Skibo, in particular, were responsible for the publication of many articles dealing with the mechanisms by which ceramic use-alteration and burial can affect the surface characteristics, weathering, and preservation of ceramics (Schiffer and Skibo 1989; Skibo 1992; Skibo and Schiffer 1987; Skibo, et al. 1989). As questions about the overall impact of burial began to arise, several studies were conducted to examine the possibility that burial conditions might have an effect on chemical composition and ceramic weathering. Reid (1984) investigated the susceptibility of fiber-tempered ceramics to damage from freeze-thaw cycles, and found that they were readily subject to mechanical damage and loss, reducing their survival within archaeological deposits in the northern United States. Roth et al. (1980), in experiments with screen size in excavation, found that the sand tempered sherds tended to break up more readily than other ceramic types, reducing their recovery rate. Franklin and Vitali's (1985) study examining the mechanisms of ceramic deterioration in simulated burial environments remains one of the most frequently cited publications on ceramic deterioration, although the testing of modern ceramic tiles limits the broad applicability of this work to archaeological examples. They found that sherds form a protective layer during burial, and will not tend to become more damaged unless the equilibrium of the sherd or

burial environment is disturbed. Sherds with intact surfaces are described as generally unaltered and they regarded overt signs of damage as evidence that weathering had occurred.

As part of a larger project investigating the impact of reservoir creation on archaeological resources, the National Park Service sponsored a study that examined the deterioration of archaeological ceramics as a result of wet-dry cycling (Murphy, et al. 1981). The experiment utilized archaeological samples and tested a wide range of ceramic types, including fiber-tempered sherds similar to the ones used in this study. They found that within several cycles calcium, potassium, magnesium, and sodium were leached from the ceramic paste, and in 40 cycles the porosity of the sherds increased considerably, possibly indicating that some weakening of the fabric was occurring. In ceramic samples fired at 600°C, the sherds disintegrated completely after 10 cycles, indicating that under-fired pieces might be quickly lost within the archaeological record if subject to similar conditions. Several studies also examined the effect of burial on potential thermoluminescent dating of ceramic materials, or the possibility of using ceramic alteration layers for dating, and have outlined the broad processes by which ceramics deteriorate during burial (Freestone, et al. 1985; Purdy and Clark 1987).

While the focus of many of the previously mentioned studies has been on the preservation of low-fired ceramic assemblages, the topic of ceramic deterioration is not exclusively limited to that of low-fired sherds. Several publications have also addressed the chemical alteration of high-fired ceramic materials in burial (Middleton and Cowell 1993; Owen and Day 1998). Owen and Day (1998) investigated the chemical weathering of soft-paste porcelains in their work at an English porcelain factory site. This study examined the selective leaching of materials from the ceramic pastes, and found that unglazed pieces were subject to weathering, while glazed examples were largely protected from chemical alteration in burial.

In the last two decades, there have been several publications broadly addressing the deterioration of inorganic materials, with some consideration of ceramic materials (Freestone 2001; Vandiver, et al. 1992). A large amount of research examining the corrosion of modern ceramics has been published in response to the need for nuclear waste containment. These have generally been attempts to predict future corrosion, but have also used archaeological examples as parallels for modern ceramic deterioration (Clark and Zois 1992). These studies typically deal indirectly with the issue of ceramic preservation.

In recent years, there has been renewed interest in the specifics of ceramic weathering processes as it relates to the chemical composition of sherds, enabled by developments in analytical technology in the intervening years. These studies differ from earlier work in that they focus not only on the chemical composition of the sherds, but the ways in which the burial environment has affected this composition. Research has focused primarily on the leaching and loss of specific elements, but like the early research of the 1960s, these studies are primarily concerned with the relation of chemical content to production areas (Buxeda I Garrigós 1999; Buxeda I Garrigós, et al. 2001; Buxeda I Garrigós, et al. 2002; Schwedt, et al. 2004; Schwedt, et al. 2006). The studies generally fall into two broad categories, profile-based or comparative. Profile studies examine the composition of prepared ceramic cross-sections, while comparative studies look at overall difference in the composition of an entire assemblage, using statistical analysis to determine significant variations.

There has been a wide disparity in the way that ceramic deterioration is addressed in academic publications, with some acknowledging and investigating the possibility, and others disregarding the concept. Apart from these publications, the post-depositional processes affecting ceramic materials have been largely ignored in archaeological and archaeometric literature, although

some have noted the need for continuing analysis in considering the impact that these processes might have on ceramic research.

DETERIORATION OF OTHER MATERIAL TYPES

Parallel research into the specifics of the burial environment and the possible effects on artifacts contained within them has been growing in number in recent years. Beginning with Schiffer's (1987) pioneering discussion of the formation processes occurring at archaeological sites, and the effects that these processes have on artifacts contained within the soil, work has continued to better characterize and understand these processes (Pollard 1998; Raiswell 2001). Studies in the deterioration of metals have included extensive discussions of the exact conditions of the burial environment, the transport of water and ions, and the types of corrosion that can be expected in a given burial environment (Geilmann 1956; Mattsson, et al. 1996; Romanoff 1957; Scott 2002). Studies of bone have focused largely on quantification of the severity of degradation in order to estimate differential preservation and with it the projected amount of original material (Beisaw 1998; Gordon and Buikstra 1981; Jans, et al. 2002; Marean 1991). There has been a fair amount of attention paid to the deterioration of archaeological glass – which has some parallels to ceramic deterioration (Doménech-Carbó, et al. 2006; Purdy and Clark 1987).

BURIAL ENVIRONMENTS

One of the most extensive discussions of burial conditions can be found in Garrels and Christ (1990), which includes a discussion of geochemical models for burial conditions, the relationship of eH and pH in soil solutions, and the stability and solubility of ions and minerals in burial. Specific attention is paid to the weathering of calcium carbonate in burial and carbonate

equilibria in soil solutions. While the impact on archaeological materials is not directly addressed, this work provides models that can be applied to the understanding of the soil environment and used to infer possible reactions and post-depositional conditions.

The unique burial environment of shell middens have been investigated by a small group of scholars primarily focused on the northwest coast of the United States (Morey, et al. 2002; Stein 1982; Stein 1984; Stein 1992; Sullivan 1994). Stein's publication "Deciphering a Shell Midden" (1992) remains the most extensive discussion of the burial environment of shell middens, although she focuses on the deterioration of faunal materials. Research into the interaction of ceramics with shell midden environments has not been addressed in any of these works due to the lack of ceramic remains within northwest coast middens.

Conservation publications addressing the specifics of burial environments have also grown in recent years, spurred by the growth of interest in the in situ preservation of materials (Caple 2004; Pollard 1998). There is now a periodic conference entitled the Preservation of Archaeological Remains In Situ (PARIS) that broadly covers issues of preservation during burial. Contributions to this conference have sometimes addressed the particulars of the burial environment. Probably the most expansive research into the effect of burial on artifacts is the Woodland burial study. Organized in the United Kingdom by the English Heritage and Forest Research Departments, this project has sought to understand the effects of burial conditions on artifacts through burial of simulated archaeological materials and long-term monitoring of the exact burial conditions surrounding them (Graham and Crow 2010). These studies, while generally in the early stages of research, are promising in their broad investigation of burial environments and potential impact on conservation research.

CHAPTER IV: METHODOLOGY

The methodology for this study was designed to characterize the chemical and physical characteristics of the selected ceramics, the degree of deterioration present, and differences present between and within the sample groups. Analysis was organized to take into consideration the limited size and high value of the artifacts. Accordingly, non-invasive means of analysis were undertaken first, because these techniques require no sampling or destruction of the object. After completion of non-invasive analysis, invasive analysis, requiring the direct sampling of material, was carried out on a limited number of sherds to complement the earlier testing. Although this sampling requires some alteration of the original sherd, the samples taken can be reused for future research if necessary. The methods and techniques used for the analysis of the sherds and accompanying soil samples are summarized in Table 1, and are listed in the order that they were performed.

Analytical Techniques	
Non-Invasive and Non-Destructive	<ol style="list-style-type: none">1. Visual Examination and Binocular Microscopy2. Portable X-Ray Fluorescence3. Variable Pressure Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectrometry
Invasive and Destructive	<ol style="list-style-type: none">4. Thin-Section Petrography5. Soil Analysis

Table 1: Techniques used for analysis.

VISUAL OBSERVATION AND BINOCULAR MICROSCOPY

Sherds were first examined visually in order to assess their overall condition and deterioration state. To standardize the classification, sherds were characterized based on eight deterioration phenomena: surface cracking, surface deposits, gloss, color alteration, erosion, loss, powdering, and structural cracking. The presence or absence of gloss and color alteration was noted. For the remaining deterioration types, the severity of the deterioration was determined based on the total area of the sherd affected. Sherds with less than one-third of the surface affected were classified as having minor deterioration, those with between one-third and two-thirds affected were classified as moderate, and those with more than two-thirds of the surface as severe. A numerical value was assigned for each level of severity, and the combined totals were used to classify the sherds as in excellent, good, fair, poor, and failing condition. A full description of the classification strategy can be found in Appendix C.

During this process, each sherd was examined using binocular microscopy to understand the surface phenomena further. Photomicrographs detailing each type of deterioration feature are included in a visual glossary in Appendix A. Images were taken using a Keyence VHX digital microscope.

PORTABLE X-RAY FLUORESCENCE SPECTROSCOPY

Portable X-Ray Fluorescence spectroscopy (pXRF) was used to examine the elemental composition of the ceramics and the paired soil samples. Each sherd was examined using a Bruker Tracer III-V, at 40 kV and 1.35 μ A, under vacuum and with no filter for 120 seconds. Four readings per sherd were taken in two locations on the exterior and interior surface of each sample. The four

readings were then averaged to minimize potential variations in the spectra recorded on a single sherd. Readings were also taken on ten cross-sections made during the thin-section process – discussed below – as a measure of the composition of the paste, and for comparison with the surface measurements. Three readings were taken on each of the ten cross-sections and were averaged to minimize variation within each cross-section. All of the spectra were deconvoluted and normalized to remove the background before proceeding with analysis of the results.

As a comparison to the results of this analysis, measurements were also taken using a Niton XL3t GOLDD+ portable X-Ray Fluorescence Spectrometer. This device provides a direct value for the concentration of analyzed elements, calculated within the device during the capturing of data. The Niton spectrometer was used on the ten sherds sectioned for petrographic analysis, on both the surface of the sherd and the bulk. Two readings were taken on each surface, for four surface readings, and three readings were taken on the cross-section, in the same manner as analysis using the Bruker pXRF. While the results from the two devices are not directly comparable, the measurements with the Niton pXRF offer additional information that can be used to support conclusions reached using the Bruker device.

These devices are able to detect a wide range of elements, many in very low concentrations, but also have important limitations. Both pXRF spectrometers have window and beam sizes that measure approximately 8 to 10 mm across. The window sizes are sufficiently wide to cover a large portion of each sample's surface, making precise readings of specific areas of interest difficult. Despite this, the beam size is also an advantage for this line of research, as the measurement of a broad area minimizes inherent variation in the heterogeneous ceramic samples. The devices primarily measure the surface of the sample, with the depth of the reading depending on the density and composition of the materials and variations resulting from surface deposits and compositional

variability of the samples. Measurements are not an accurate representation of the bulk composition of the sample when taken on the surface of a sample rather than a cross-section. The geometry of the sample can also affect results, and data is most reliable when performed on flat samples. Analysis is also limited in its detection of light elements, and elements of very low concentration. The Bruker is not capable of detecting elements lower in atomic number than aluminum, while the Niton cannot detect elements lower than magnesium.

Data from the Bruker device was examined using the peak area for each element as a proxy for element concentrations. Counts are obtained by the device that correspond to the number of x-rays recorded by the detector and represent the concentration of the element. The number of counts is plotted versus energy level, forming a characteristic peak for each element. The area underneath this peak is then the integrated number of counts for a given element. The ratios of these peaks were compared in region of interest analysis to understand the relative concentration of each element. Error was calculated to 2σ , a 95.4% confidence interval. The concentrations of elements are directly provided by the Niton device, therefore the part per million (ppm) concentration of each element was plotted, and region of interest analysis was unnecessary. Error values of 2σ are calculated within the device and given for each reading.

VARIABLE PRESSURE SCANNING ELECTRON MICROSCOPY, COUPLED WITH ENERGY DISPERSIVE X-RAY SPECTROSCOPY

Variable pressure scanning electron microscopy (VPSEM) was used to investigate the ceramic surfaces and cross-sections at high magnification. Observations and analysis were carried out with a FEI Nova NanoSEM 230 equipped with an energy dispersive X-ray spectrometer (EDS), in both secondary (LVD detector) and backscatter (GAD detector) electron modes. EDS was used

to analyze the elemental composition of the ceramics and to map elemental distribution in areas of particular interest. This is especially useful for detailed examination of surface features and spatial variation in the composition of the sherds. Images showing variations in topography and surface features were acquired in secondary electron mode, while backscatter electron mode was used for elemental analysis and mapping. The latter provides spatially resolved imaging based on the differences in atomic weight and elemental concentrations across the analyzed surface of a sample.

The VPSEM-EDS is capable of detecting light elements such as sodium, magnesium, and aluminum and therefore complements the data collected with the pXRF. As with pXRF, EDS analysis can be affected by variations in surface topography and functions best when performed on flat samples.

THIN-SECTION PETROGRAPHY

Thin-section petrography is a technique conventionally used for the analysis of ceramic materials because it provides a detailed understanding of the texture and the nature of the various mineralogical components and constitutive phases of the ceramic paste. Prepared slides of ceramic thin-sections can be examined using a polarized light microscope with transmitted light, and the optical properties of the grains can be determined for the identification and characterization of the ceramic paste and inclusions. Properties such as porosity and the preparation of the clay can also be studied. Thin sections were prepared by slicing the sherd and fixing the freshly cut surface to a glass slide with epoxy resin, followed by grinding and thinning down to a thickness of approximately 30 to 40 microns, a standard thickness for petrographic analysis. Ten sherds were selected for thin-sectioning, three from the shell-free area, and seven from the dense shell. The sherds were selected

based on the level of preservation determined in earlier examination and were chosen to represent as wide a range of locations within the units as possible.

EXAMINATION OF SOIL SAMPLES

Paired soil samples, taken from each level with associated sherds, were examined for chemical composition, salt content, and pH values. This information was collected to compare with the chemical constituents and observed weathering patterns of the sherds contained within each level. Each soil sample was dried for 24 hours prior to any analysis, as recommended by Tan (1996). Samples were then sieved, using 2 mm mesh, to remove the heavy fraction prior to analysis. After removal of samples from the ground, remaining moisture can promote continued chemical and biochemical reactions that can distort subsequent analysis. The drying process is expected to slow or stop any further reactions, although pH levels can be slightly reduced by the drying process (Tan 1996:17-19). The soil samples used in this study were originally removed during excavations in 2006, which could be a source of some error in the results. Once processed, the soils were examined for salt content, organic content, carbonate content, pH levels, and elemental composition.

SALT CONTENT

The salt content of the soil can be an indicator of the extent to which the buried ceramics are affected by potentially damaging soluble and insoluble salts. To examine the salt content, conductivity readings were taken with a Corning Duo-60 conductivity meter, calibrated with a saturated salt solution. Detection of individual salt species, including carbonates, chlorides, sulfates, and nitrates, was conducted with microchemical tests taken from Odegaard et al (2000).

ORGANIC MATERIAL

The organic material present in the soil can be an indicator of the prevailing conditions within the burial environment and the degree to which acids can be formed from the organic components. The percentage of organic material in the soil samples was measured using a loss-on-ignition test described in Stein (1984:241). A desiccated sample of the soil is heated to 550°C, with the weight loss of the sample representative of the organic components present in the soil. A detailed description of the procedure is included in Appendix B.

CARBONATE CONTENT

The carbonate content can indicate the source of water movement in a shell midden and associated leaching that might occur. Rainwater moving downward through the midden will typically leach materials from the upper levels, while groundwater percolating up into the midden will typically leach materials from the lower levels (Stein 2008:74). The percentage of carbonates was measured with the loss-on-ignition technique used to determine the organic content, and described above. For the determination of carbonate content, the samples were heated to 1000°C and the weight loss calculated to measure the carbon dioxide evolved from the sample and the carbonate content by proxy.

pH

The pH of each soil sample was tested according to the protocol given in Tan (1996:105), using a Beckman φ340 pH and Temperature meter calibrated with buffer solutions of pH 4.0 and 7.0. Measurements were recorded as pH value in water.

ELEMENTAL COMPOSITION

The soils were analyzed using the Bruker Tracer III-V and the Niton XL3t GOLDD+ pXRF spectrometers. Samples were prepared in a small plastic ring of uniform size, at a depth of approximately 3 cm, and covered with a thin film to allow the X-ray beam to hit the sample while holding the material in the container. For each soil sample three readings were taken with both spectrometers, using the procedure described previously for the analysis of the ceramic samples.

CHAPTER V: RESULTS

BROAD CLASSIFICATION OF SHERDS

The examination and classification of the sherds revealed notable differences between the sherds from shell and non-shell contexts. The sherds from the dense shell group tended to be in less stable condition, and exhibited a broader range of surface and structural deterioration (see Fig. 4). Sherds from the non-shell context ranged from excellent to fair condition, but none exhibited the extreme levels of deterioration found in the dense shell examples, as shown in Figure 5. Overall, the same deterioration features were present in both groups, but were more severe and more common in the dense shell ceramics. A detailed graph of the range of preservation within each level is included in Figures 30 and 31, in Appendix C.

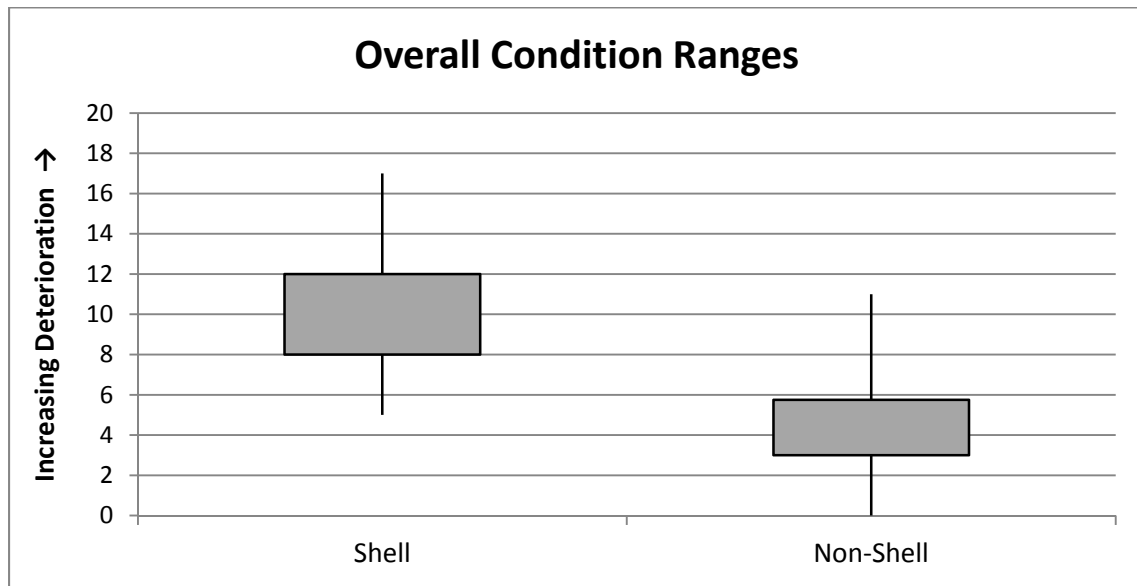


Figure 4: Overall preservation levels of ceramics within the two groups, determined according to the classification scheme described in Appendix B.

SPECIFIC DETERIORATION PHENOMENA

Instances of all deterioration phenomena except for surface cracking were more common in the dense shell than the shell-free context (see Fig. 6). Surface cracking occurred in approximately the same number of sherds from the shell and non-shell, nineteen and twenty out of thirty sherds, respectively. Surface deposits and color alteration were far more prevalent in the dense shell than the shell-free context. This is closely tied to the burial environment, and due to the close contact with the shell matrix. Other types of deterioration, such as powdering and structural defects, were far more prevalent in the dense shell examples.

Additionally, the severity of the deterioration, determined based on the percentage of a sherd's surface affected by individual deterioration types, varied greatly between the two groups. Sherds with less than one-third of the surface affected were classified as having minor deterioration, those with between one-third and two-thirds affected were classified as moderate, and those with more than two-thirds of the surface as severe. The deterioration phenomena affecting sherds from the shell-free area were mostly minor or moderate in nature. Only five of the thirty sherds from the shell-free area exhibited severe forms of deterioration. On the other hand, twenty-eight of the thirty sherds from the dense shell had one or more type of severe deterioration. Notably, 40% of the sherds had severe powdering, 30% had severe surface cracking, and 20% showed signs of severe erosion to the surface. This indicates that not only are the sherds from the dense shell more prone to deterioration, but the extent of the deterioration is also more pronounced in the samples analyzed.

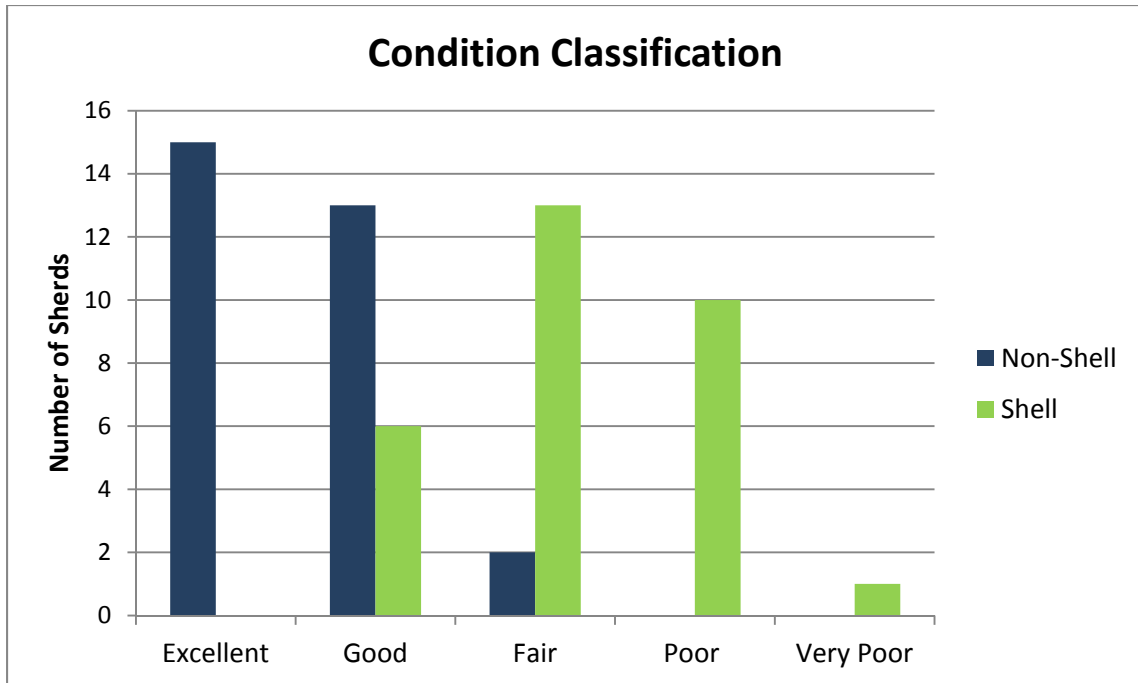


Figure 5: Classification of preservation levels.

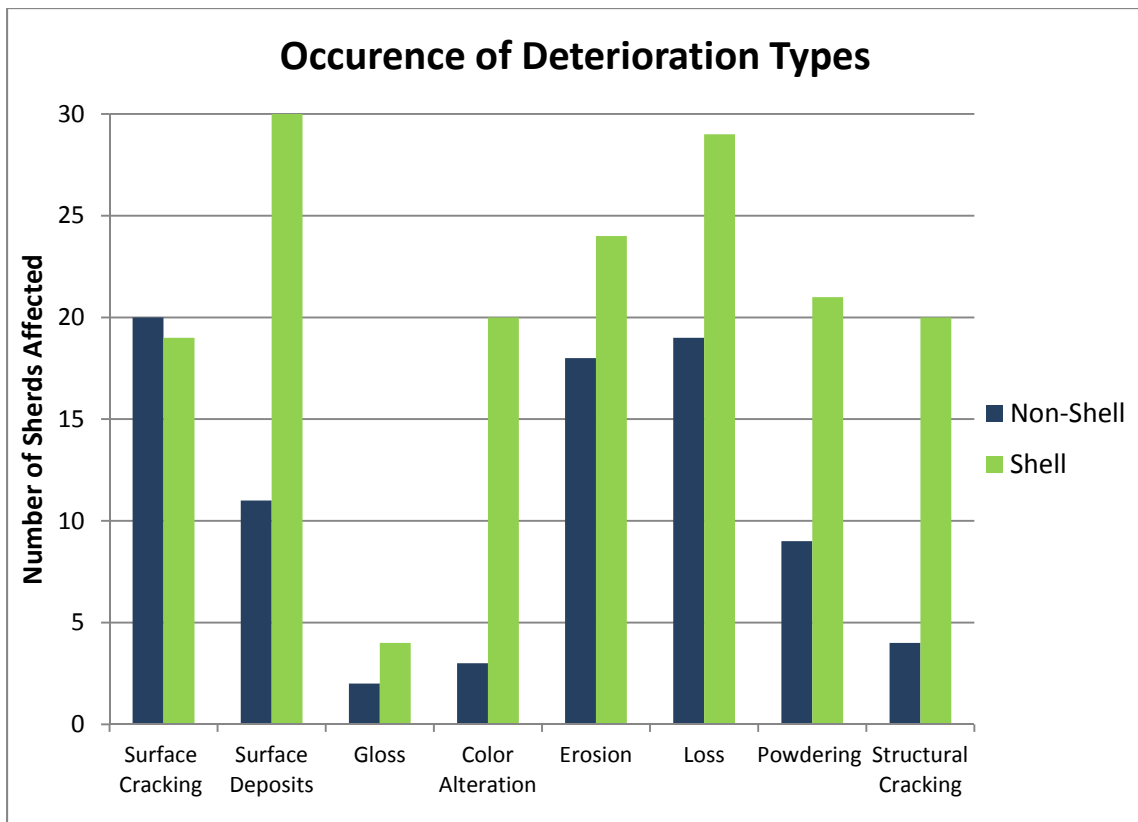


Figure 6: Occurrence of deterioration types in the two burial environments.

PORTABLE X-RAY FLUORESCENCE SPECTROSCOPY

Examination of both sample groups using pXRF indicated prominent differences in elemental composition between the surfaces and the ceramic pastes. While the elemental composition of the ceramic surfaces has shown distinct differences between the two groups, there was little variation in the paste composition of the sherds from the two burial environments as measured on the cross-sections. Elements of interest for the pXRF analysis were Ca, Ti, Si, Al, Fe, P, K, S, Mn, Zn, Sr and Zr. These were selected based on their presence in the composition of the ceramics and soils. Previous studies have noted the mobility of Ca, K, P, Mg and Na, thus these elements were of particular interest (Freestone, et al. 1985; Murphy, et al. 1981). Although important, Mg and Na were not considered in the analysis because they are beyond the detection limit of the pXRF.

The results from pXRF analysis indicated that the paste composition of the ceramics is mainly composed of Al and Si, while Ti and Si levels had significantly higher values on the surface of the sherds buried in sandy soil (see Fig. 7). Ca levels, on the other hand, were significantly higher on sherds buried in the dense shell (see Fig. 8). Zr levels were elevated in both burial environments, while Fe, and P levels were widely dispersed and considerably overlapping between the two groups (see Appendix E). Mn concentrations on the cross-sections were extremely low, but were elevated in readings of both the dense-shell and non-shell surfaces. Using the Bruker pXRF, peaks of K, S, and Zn were too low to provide confident results, and these elements were not plotted in the final data. Results from the Bruker and Niton devices were very similar, and confirmed the general trends

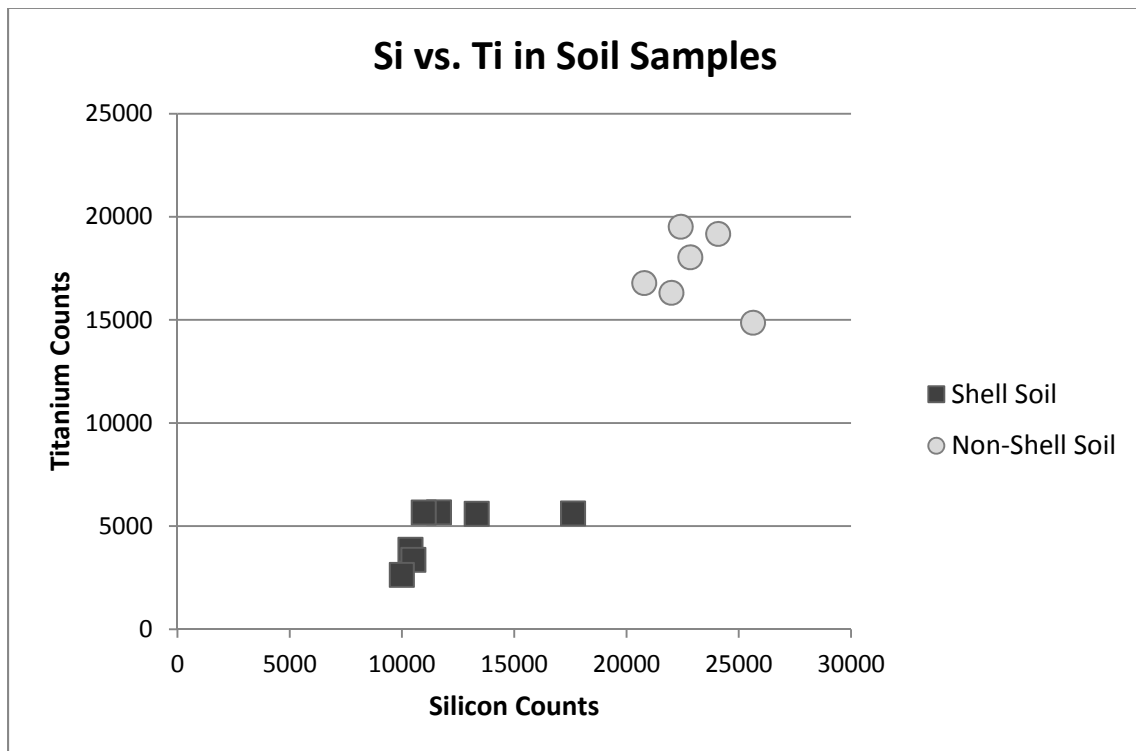
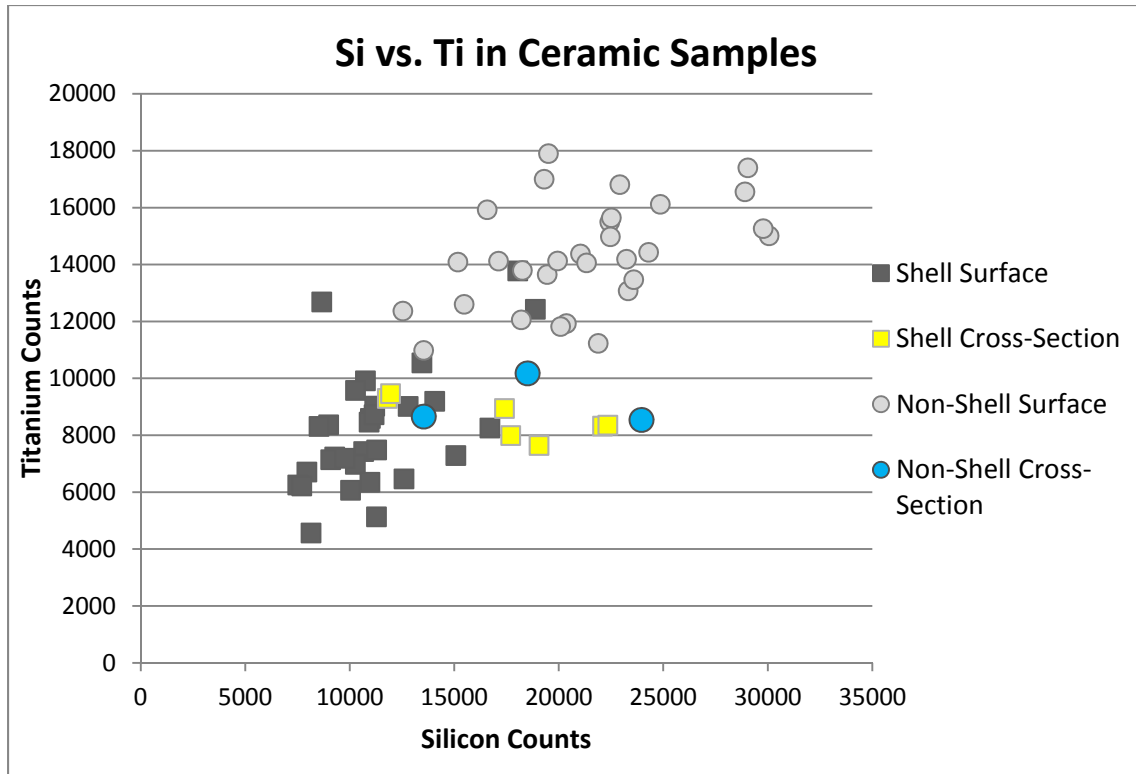


Figure 7: Silicon and titanium ratios in the Bruker pXRF results.

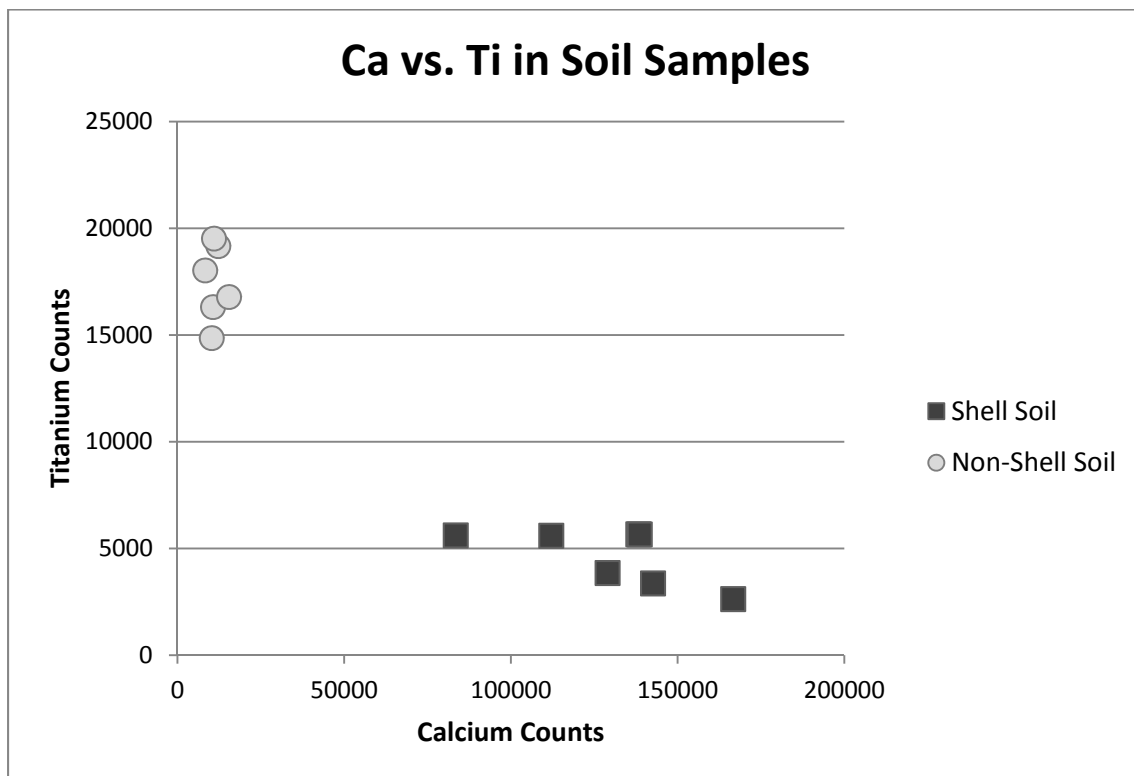
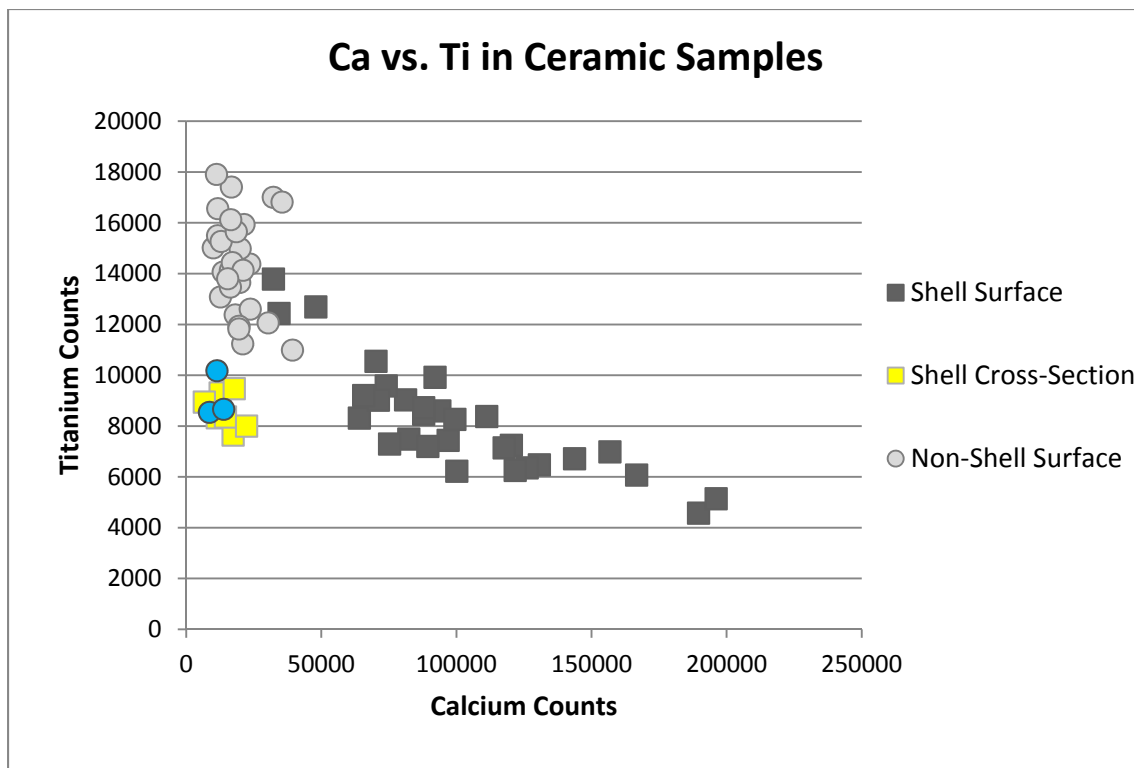


Figure 8: Calcium and titanium ratios in the Bruker pXRF results.

discussed above (see Appendix E). Overall, considerable differences were most apparent between the surfaces and pastes of the samples.

VARIABLE PRESSURE SCANNING ELECTRON MICROSCOPY, COUPLED WITH ENERGY DISPERSIVE X-RAY SPECTROSCOPY

Examination with VPSEM confirmed the findings from pXRF analysis. The bulk composition of the sherds was largely similar between the two burial environments, but substantial

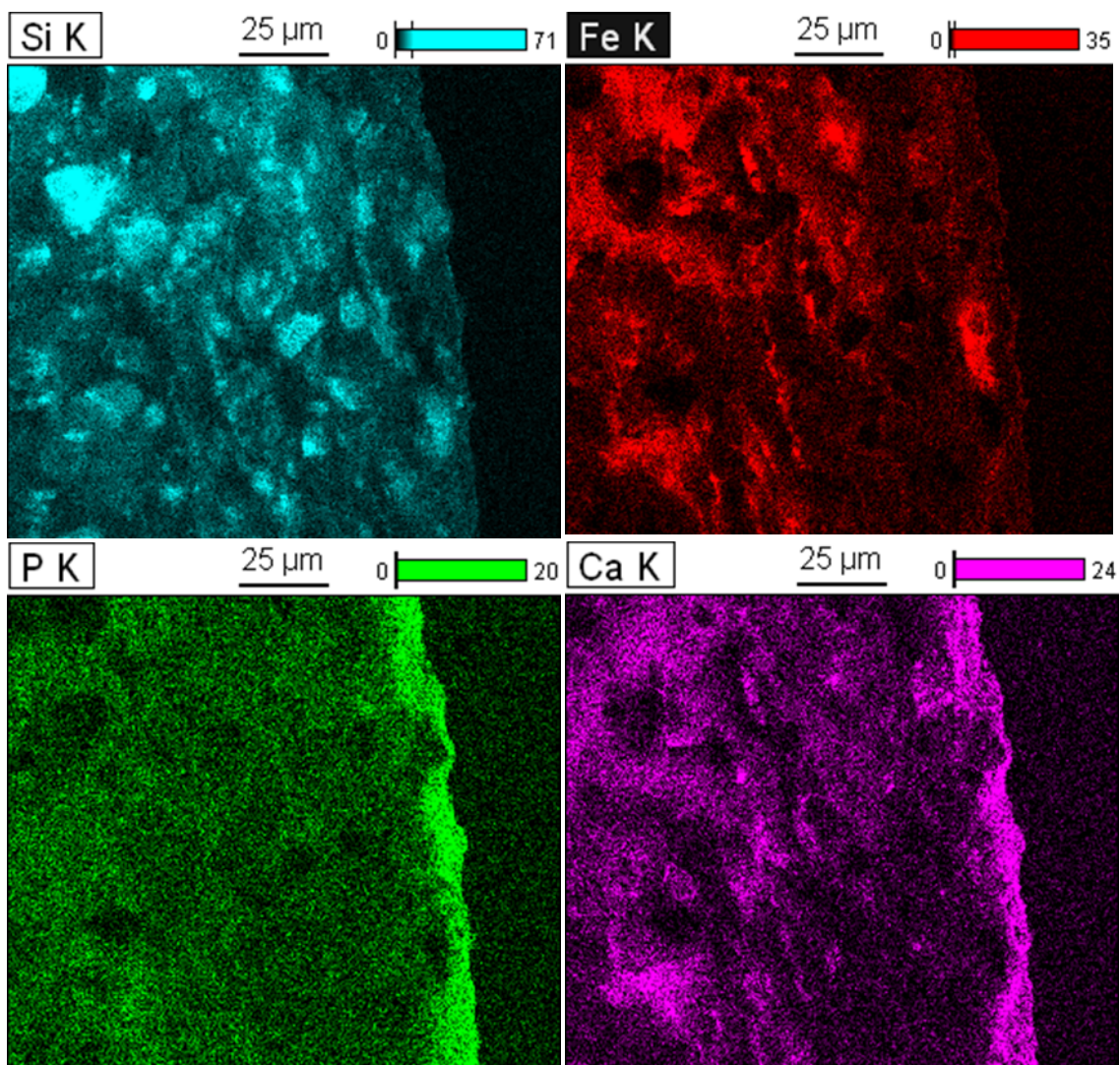


Figure 9: EDS mapping of sherd #28.4/6642, from the dense shell, taken at 2000x magnification. Concentrations of calcium and phosphorus on the outer surface and depletion of iron just below the surface are visible.

variation occurred on the surfaces. EDS was used for elemental mapping on the cross-sections, highlighting variations in the distribution of elements between the surface and the paste. These maps (shown in Fig. 9, 10 and 11) show the counts registered by the detector for a given element, with a dot of color representing the presence of the element and black areas indicating a lack of the element. In ceramics from the dense shell, distinct concentrations of Ca, P, and in some case Zr were visible on the weathered surface, generally measuring approximately 25 microns or less. Some areas had noticeably less iron just below the surface of the sherd when compared to the paste,

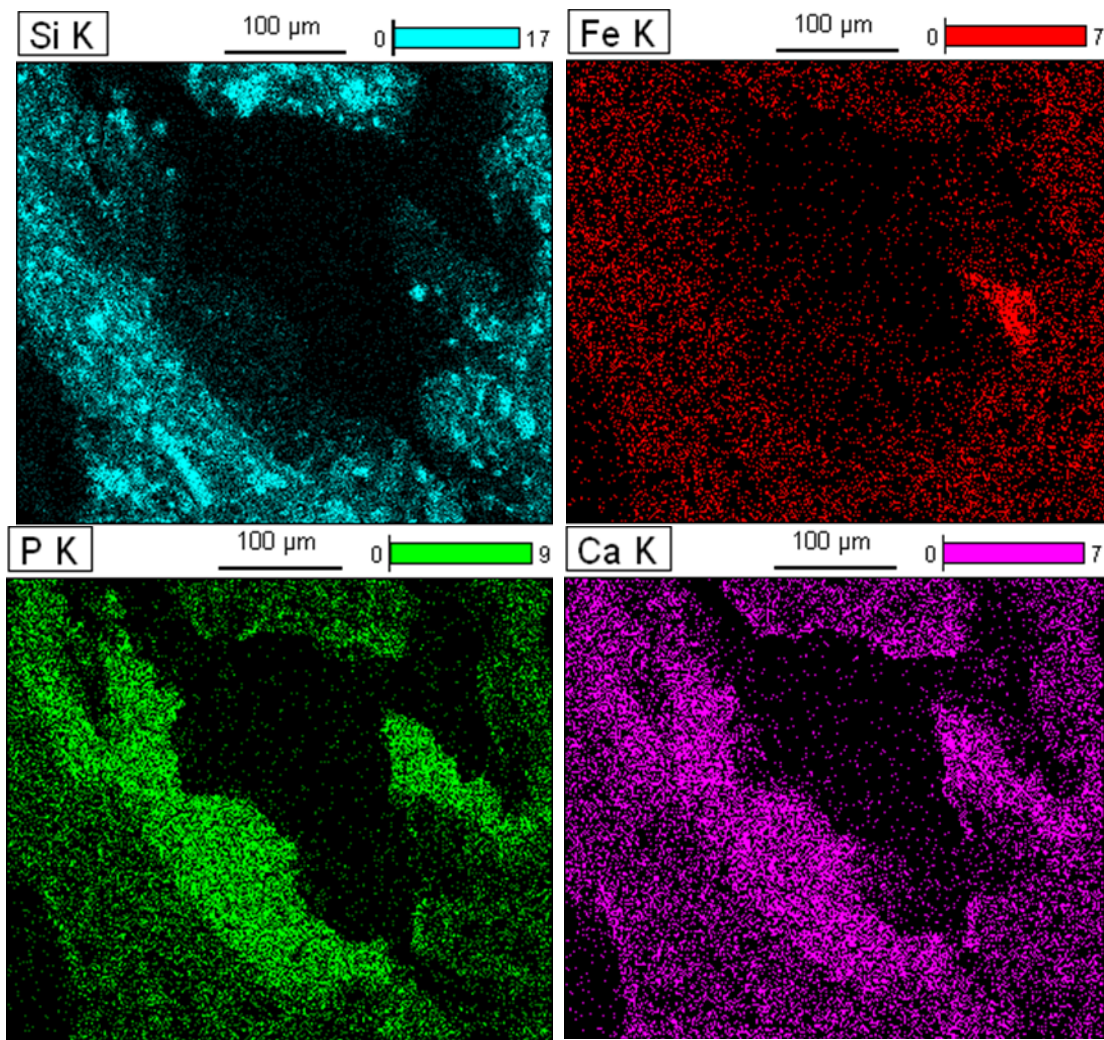


Figure 10: EDS mapping of sherd #28.4/6301, from the dense shell, taken at 708x magnification. Concentrations of calcium and phosphorus are visible around the edge of the pore

while Ca and P were mapped lining pores of the ceramics from the dense shell group. These were primarily located in close proximity to the outer edge of the sherd. In the ceramics from the shell-free group, there were typically not distinct surface layers (Fig. 11). There were some instances of heavy iron concentrations lining the pores, somewhat similarly to the Ca and P concentrations found in the dense shell examples. There were not similar concentrations of Ca and P in the pores of the sherds from the sandy soil.

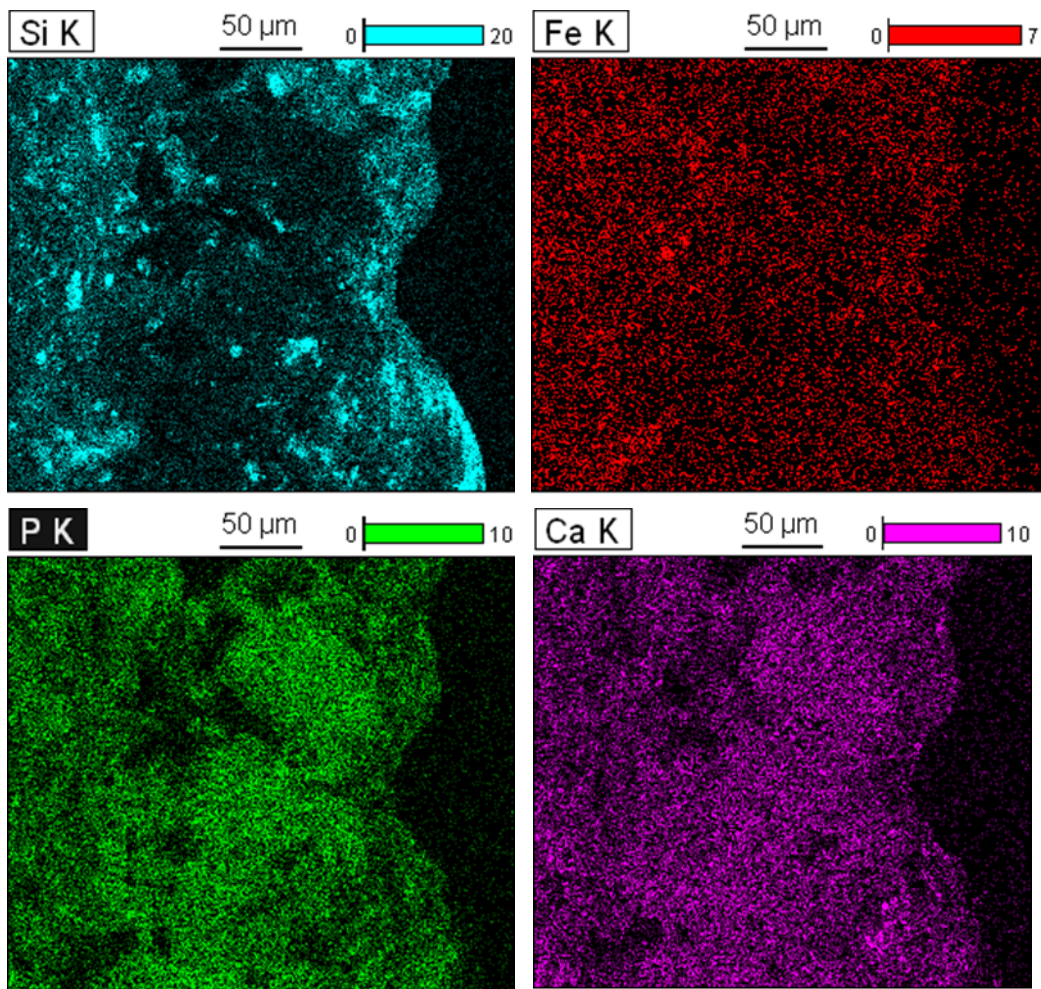


Figure 11: EDS mapping of the edge of sherd #28.4/5219, from the non-shell soil, taken at 500x magnification.

THIN-SECTION PETROGRAPHY

Petrographic characterization of the ceramic thin-sections using polarized light microscopy (PLM) indicated great variability in both the composition and condition of the sherds. While all sherds have a high quartz (SiO_2) content, and small quantities of feldspars, mica, and amphiboles, the organic tempering component is variable. In some samples, a dense concentration of elongated voids is present from the combustion of the organic components, while others had very little (see Fig. 12 and 13). The carbonized remains of the organic fibers used for temper are still present in some the voids and visible in the thin-sections. In some areas, the quartz grains are aligned due to the working of the clay in production. The ceramics in the dense shell show indications of precipitated calcite (CaCO_3) in many of the pores, especially those near the surface of the sherd (see Fig. 14). This could potentially be gypsum (CaSO_4) as well, although concentrations of sulfur were not detected using other analytical techniques. Calcite was also visible lining small fissures along

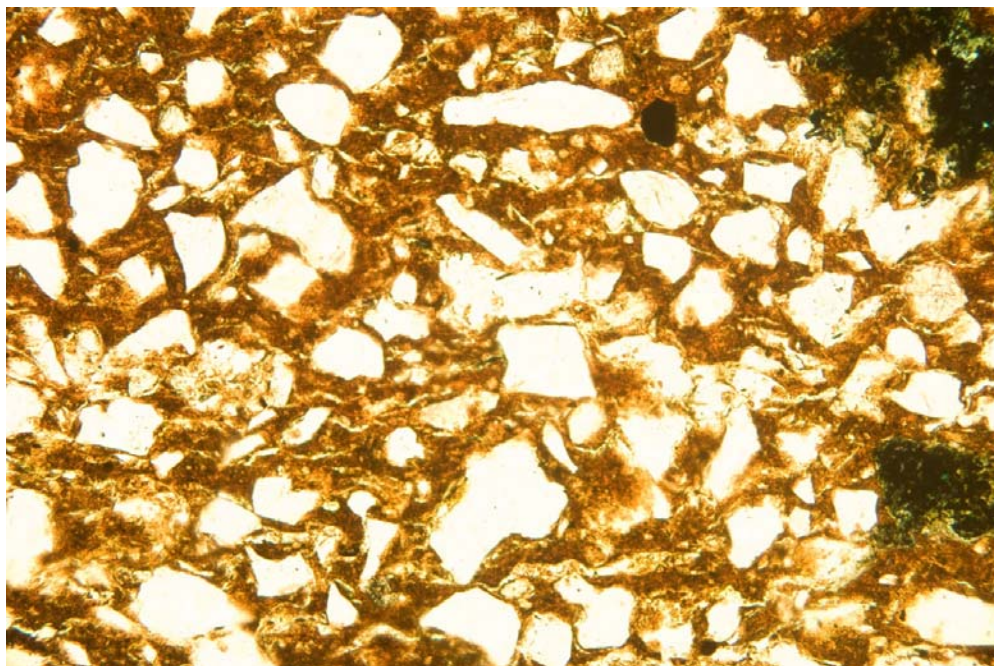


Figure 12: An example of the bulk composition of the ceramics, showing the heavy quartz tempering.

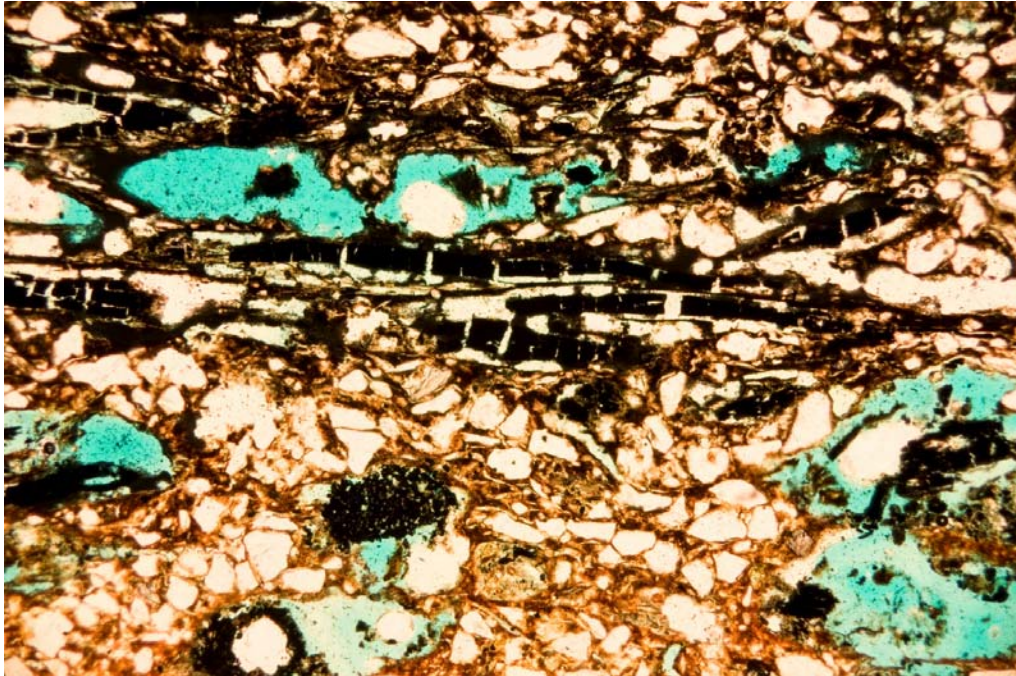


Figure 13: Carbonized organic remains visible in the pores of a sherd.

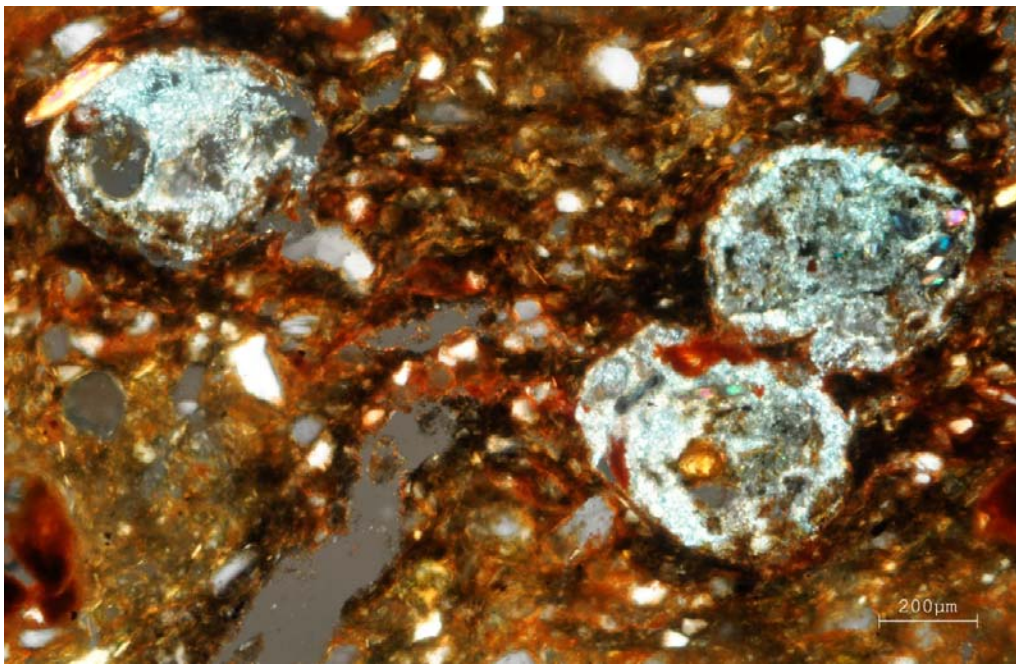


Figure 14: Calcite deposits in the pores of sherd #28.4/6642, from the dense shell

the surface of several sherds. In many of these there is a heavy concentration of what appears to be iron oxide (Fe_2O_3) as well, forming a ring around the pore itself. In some instances there seems to be iron oxide precipitated along with the calcite.

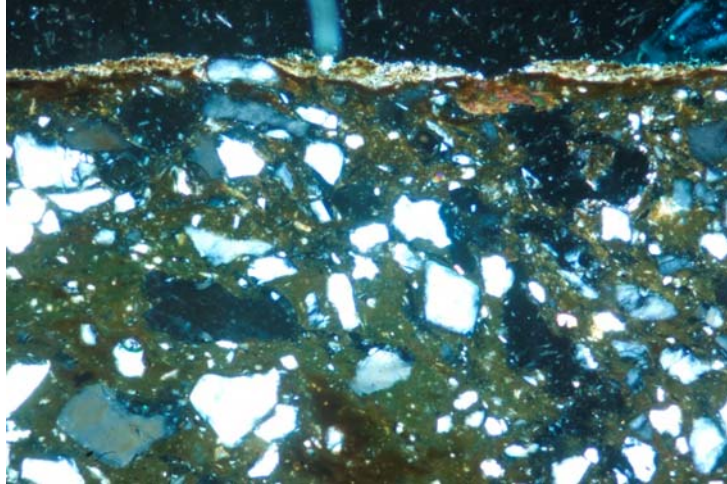


Figure 15: A precipitated calcite deposit on the surface of sherd #28.4/6012, from the dense shell group.

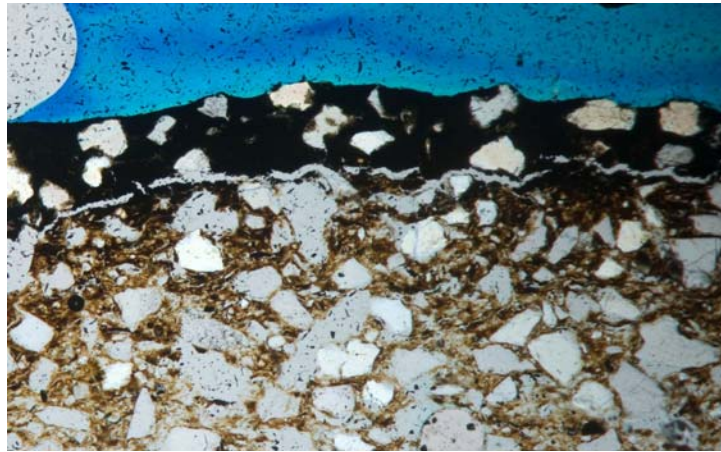


Figure 16: The glossy surface deposit on sherd #28.4/5961 from the dense shell group.

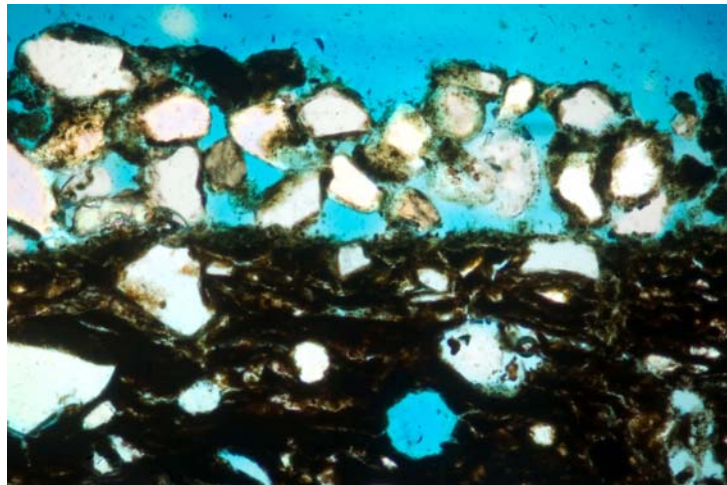


Figure 17: Surface deposits on sherd #28.4/5219, from the shell-free sandy soil.

Discrete layers were also visible on the surface of many of the ceramic thin-sections, both on those that have visible surface deposits and those that do not. Most of these layers are composed of precipitated calcite, and often shell fragments are embedded in the weathering layer. This seems to be typical of the weathered surfaces, as seen, for example, on sherd #28.4/6012 (see Fig. 15). Alternately, the glossy surface of sherd #28.4/5961 is visible as a discrete dark layer, and varies considerably from the precipitated calcite layers of the other sherds from the dense shell group (see Fig. 16).

The sherds from the sandy soil did not show the same surface layers, but they did display visible surface deposits. Sherd #28.4/5219 had thick deposits on the surface, composed largely of quartz, but also containing some other small grains (see Fig. 17). There were some concentrations of iron oxide visible on the surface of this sherd as well.

SOIL TESTING

Soil samples indicated considerable variability both between the units tested and within each unit. The percentage of calcium carbonate, as measured through loss-on-ignition testing, was considerably higher in the shell deposits. In the dense shell unit N784 E797 the amount was highest in the uppermost stratigraphic level tested (approximately 10 cm below the ground surface), and decreased to the lower levels (approximately 70 cm below the surface), ranging between 35% in the upper level and 20% in the lowermost level. Only two levels were tested in dense shell unit N784 E811; here the upper level was slightly higher in carbonate content than the lower level, at 31% and 29% respectively (see Fig. 18). In the shell-free sandy soil, weight loss during firing was extremely low, corresponding to possible carbonate content between 0.65% and 1% in the samples (see Fig. 19). Spot tests for carbonates in the non-shell sandy soil were negative, indicating the absence of

carbonates in the soil or amounts lower than the detection levels of the test, between 3 and 7%. Unit N779 E801, in the non-shell sandy deposit, had lower organic content, ranging from 1.5 to 3%. Conductivity readings in all of the units were relatively low, suggesting that soluble salts are not common within the soil. All of the soil samples had adjusted values¹ lower than those given as an acceptable stopping point for removal of salts from ceramics, implying that the salt content is not high enough to be damaging to the ceramics contained within the soils (Unruh 2001). Microchemical spot tests for sulfates and chlorides were negative for all soils, in both the dense-shell and shell-free sandy soils. Nitrates were detected in all of the soil samples, from both burial environments (see Appendix D, Table 9). The conductivity of the soil within the dense shell seems to be correlated to the calcium carbonate concentrations, indicating that calcium carbonate is largely responsible for the conductivity levels in this area. The shell-free soils do not follow this same pattern – the small amount of weight loss observed (1% and below) prevents the determination of a similar pattern in this area.

The pH levels varied somewhat between the dense shell and shell-free units, but did not vary considerably within each individual unit (see Appendix D, Table 7). In the shell-free unit, the readings all fell into the neutral or slightly alkaline category², ranging between 7.1 and 7.5. As expected, the dense shell soils were consistently more basic than the sandy soils, and all fell into the moderately alkaline category, ranging between 7.9 and 8.3 among the samples tested. In unit N784 E797, the soil became more alkaline in the deeper levels, but the changes were very slight. As

¹ Taken from desalination procedures used to determine the acceptable level of salts present in solution, in the context of the desalination of archaeological ceramics. Adjusted values are determined based on the formula $k_{adj} = k(L)/gm$; where k_{adj} is the adjusted conductivity value, k is the conductivity reading obtained using a conductivity meter, L is the volume of water used for testing, and gm is the weight of the sample. Using k_{adj} values instead of reading directly from a conductivity meter standardizes the testing procedure and allows for comparison of samples with different weights (Unruh, 2001).

² As defined by the USDA Natural Resources Conservation Service (USDA 1998).

previously noted, there is some possibility of error in these readings due to the length of time that elapsed between collection of the samples and analysis.

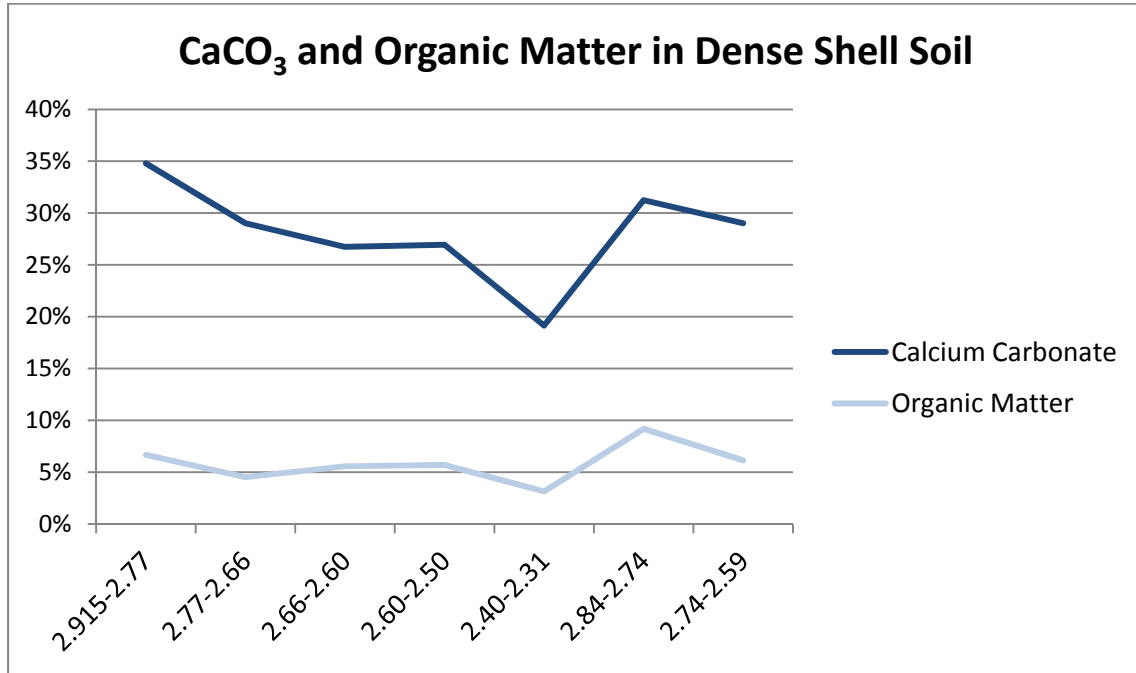


Figure 18: Calcium carbonate and organic matter composition in the dense shell areas.

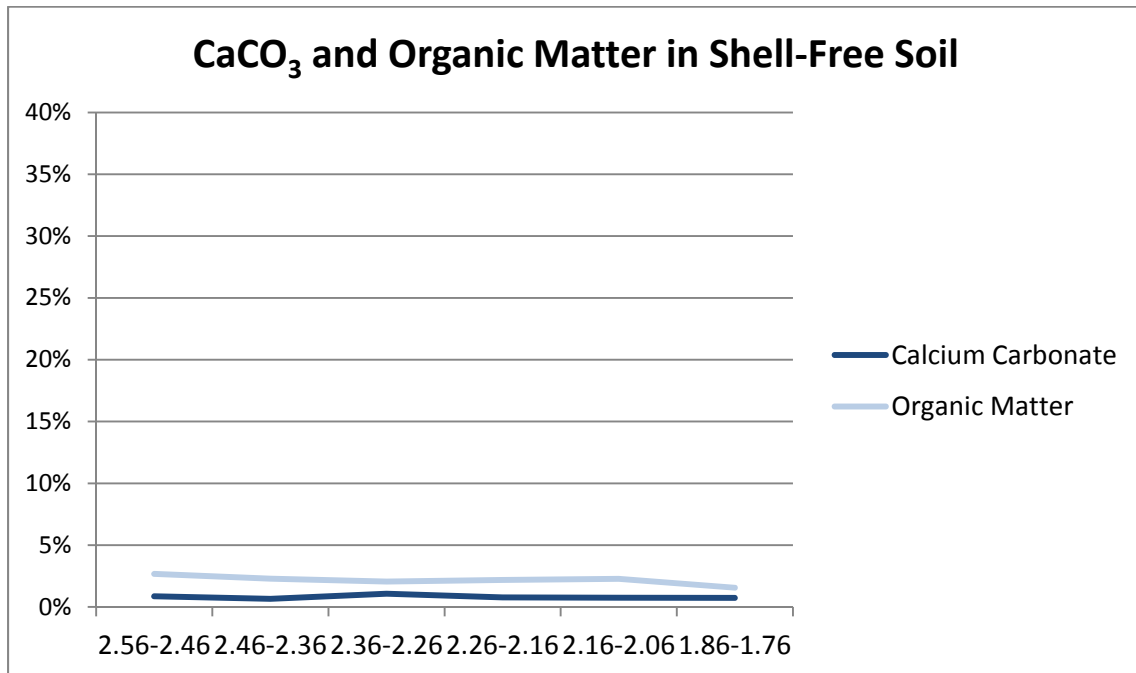


Figure 19: Calcium carbonate and organic matter composition in the shell-free area.

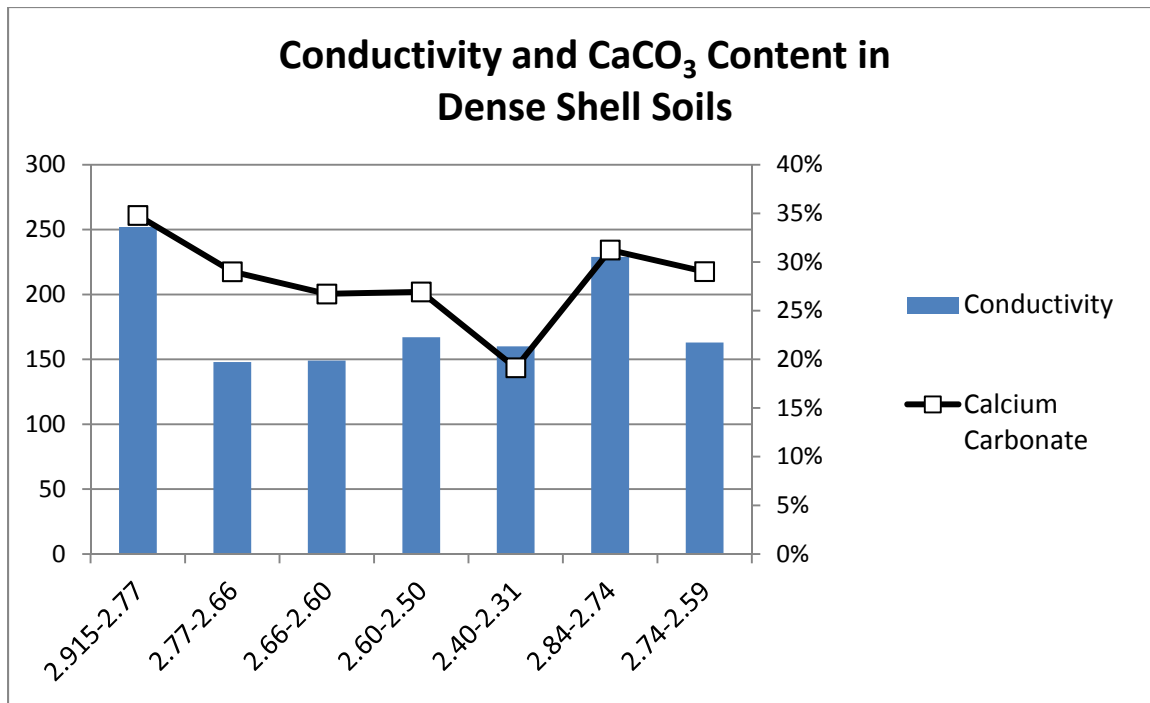


Figure 20: Relationship of conductivity to calcium carbonate content in the dense shell environment.

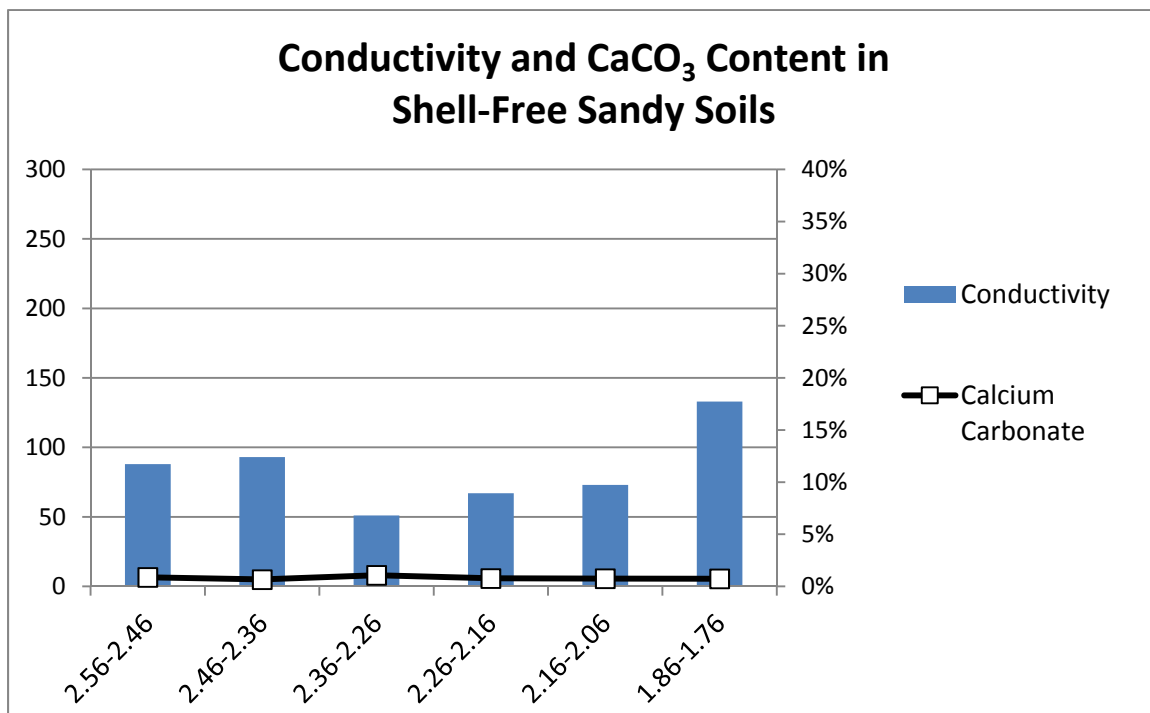


Figure 21: Relationship of conductivity to calcium carbonate content in the shell-free environment.

CHAPTER VI: DISCUSSION

CONDITION OF SHELL VERSUS NON-SHELL ARTIFACTS

The frequent occurrence of surface powdering in the dense shell group – more common than in the shell-free samples – indicated excessive loss of cohesion on the surface of the sherds buried in a shell-rich environment. The high instance of structural cracking in the dense shell as compared to the shell-free group also indicated that the structural weakness of a number of sherds extended beyond the surface. It is possible that the sherds analyzed in the course of this study represent different stages in the deterioration process, depending on the exact conditions to which they were subjected during burial. The occurrence of surface erosion and loss of the sherds' fabric was common in both the dense shell and shell-free areas, perhaps due to actions taking place in both burial environments.

The movement of water within the burial environment seems to be largely responsible for the changes in elemental composition and likely for the varied condition of the sherds as well. Murphy et al. (1981) found that calcium, sodium, magnesium, and potassium were the most frequently leached elements from archaeological ceramics subject to long-term soaking in water. While limits of the instrumentation restricted the analysis of sodium and magnesium, other elements can also provide indicators of the movement of water. Phosphorus and iron are also potentially highly mobile elements given the appropriate chemical environment in burial (Maritan and Mazzoli 2004; Pillay, et al. 2000:55-58). The presence of precipitated calcite and phosphorus concentrations within the pores of the ceramics confirms that the flow of water within the burial environment is having some impact on the composition of the sherds. Another possible result of the action of water is the loss of iron close to the ceramic surface. If the mobile calcium and phosphorus are dissolving

and precipitating in cycles with the movement of water, this could be related to the deterioration seen here. The flow of water within the midden and the sandy soil is then of primary importance when examining the condition of these materials. The difference in condition of sherds within a single level, and the variety of deposits formed on the surfaces of many of the sherds also attests to the complexity of the burial environment.

A direct correlation between the soil pH values and the condition of the sherds in individual levels was not apparent, aside from the broad differences found in the dense shell and shell-free soils. The small sample size used in this study limited fine-grained analysis of correlations that might be apparent with a larger sample size, but this does not rule out the impact of soil pH on the processes taking place. The difference in pH values between the two burial environments should nonetheless affect the availability of ions in the soils, and thus the materials that are deposited into or leached from the sherds.

pXRF analysis has indicated that the elemental composition of the ceramic surfaces is closely correlated with the conditions of the burial environment. This was apparent on surfaces that are not visibly weathered or covered with surface deposits. pXRF has also indicated that the paste composition of the sherds was not accurately represented by readings taken on the surface of the sherds. While the material deposited on the surface does not appear to penetrate deeply into the fabric of the sherd, there is significant movement of materials through surface fissures and pores within the ceramic body. The high correlation of calcium and titanium content of the sherds when compared with the soil samples has indicated that changes in the ratio of these elements was related to the material deposited on the surfaces of the ceramics. The titanium content was higher in the sandy non-shell soil, while the calcium was higher in the dense shell deposits. Notably, this seems to be the case in all of the sherds tested, regardless of whether deposits were visible on the surface.

This indicates that a visual inspection alone is not enough to confirm the alteration of the surfaces from burial, but that finely deposited materials or alteration layers can potentially be detected by some analytical equipment.

The distribution of calcium carbonate in the dense shell deposits indicated that inundation of the midden is not coming from rainwater moving from the surface level down through the shell deposit. If this were the case, it would be expected to observe leaching of calcium carbonate from the shells in the upper levels, gradually decreasing through the deeper levels. Instead the opposite pattern is present, indicating that dissolution of the carbonate content is occurring in the bottom of the midden, presumably through interaction with groundwater (Stein 2008:76). Inundation of the site should affect sherds in both burial environments, but the differential preservation of the ceramics indicates that this factor alone is not causing the deterioration. Were it the case, sherds buried in lower levels and most affected by rising water tables would be expected to show more severe forms of deterioration, but sherds in the lowest levels were in good states of preservation. In order for water to be capable of dissolving the calcium carbonate of the shells, or potentially within the ceramic body, carbon dioxide must be present in the water. This is a common occurrence, but can only be sustained in moving water; stagnant water will be rapidly depleted of the necessary carbon dioxide and rendered incapable of dissolving the soluble materials (Buys and Oakley 1996:27). With this in mind, it is likely that the water is moving through the burial environment frequently enough to inundate the area, and enough to saturate the contained artifacts.

EFFICACY OF ANALYTICAL TECHNIQUES

The use of complementary non-invasive analytical techniques proved to be valuable in the

determination of deterioration patterns and compositional assessment. The broad range of elemental detection possible with VPSEM-EDS complemented the pXRF analysis, which is limited in the detection of light elements. Non-invasive pXRF analysis was especially useful in comparing the composition of the paste with the surfaces of the ceramics. It was necessary to have freshly cut surfaces for comparison, as surface readings are limited in their ability to provide information about the composition of the paste. Here it is important to consider that under some circumstances, weathering could also affect the core, and the analyzed composition might differ from the original one. The surface readings instead provide information about the alteration layer present on the ceramic surface and the burial environment of the ceramic. It was therefore most productive to combine the use of non-invasive pXRF and VPSEM-EDS with the invasive thin-sectioning process. Thin-section petrography was able to provide information about the nature of these alteration layers, as well as the mineralogical assemblage and the texture of the ceramic body. Limitations due to sample geometry, for both pXRF and VPSEM-EDS, also made the use of smooth, freshly cut sections more reliable for compositional data than an uneven weathered surface or even a freshly broken but uneven surface. The exclusive use of non-invasive techniques proved insufficient to answer the research questions posed here, due to limitations of the techniques and the altered nature of the samples. By using a restricted amount of invasive testing to confirm the results obtained non-invasively on a larger group of samples, the techniques can be combined with limited destruction of valuable archaeological materials.

IMPLICATIONS FOR ARCHAEOLOGICAL RESEARCH

The differences in condition of ceramics resulting from the differential environments occurring in burial must be carefully taken into consideration before undertaking chemical and physical analysis of the assemblage. Based on the data derived from pXRF analysis, the surfaces of

the ceramics seem to be sensitive indicators of the burial conditions. There is at times a large disparity in the proportion of elements present in the surface and interior of a sherd as a result. The bulk elemental composition of the sherds appears largely the same regardless of the burial environment, and no indications were found in this analysis to show that differences can be accounted for by ceramic use prior to burial. While pronounced differences were present between the surfaces and pastes of the ceramic samples, this does not guarantee that the composition of the paste at present is identical to the original composition.

The transfer of exogenous materials into the body of the ceramic and the leaching and dissolution of the original fabric is closely related to the burial environment, and demonstrated by differences in condition after excavation. However, the lack of change in the ratio of some elements, such as calcium and iron in the core of the sherds indicates that the degree of infiltration is limited to the outermost surfaces of the ceramics and the break edges. While trace elements, such as those typically used for provenience studies, were not examined explicitly in this study, noticeable changes in the concentration of these elements are also likely when examining the surface of archaeological ceramics. Weathering can therefore have broad effects, influencing both compositional and sourcing data. Any chemical or mineralogical comparison of materials from similar shell midden sites, or examination of low-fired ceramics should proceed with caution, and direct comparison of materials from different burial environments approached with a level of skepticism. The weathering of this assemblage, and the variable conditions of the ceramics that result, are indicative of chemical and physical changes occurring to the ceramics, but these changes are not always readily visible on the surfaces of the ceramics.

RECOMMENDATIONS FOR EXCAVATION AND STORAGE

These results highlight the complexity of predicting artifact preservation, and the variation that can occur within a single site. Accordingly, the results indicate that ceramics cannot be treated in a uniform manner, and should be evaluated on a case-by-case basis. Low-fired ceramics that appear relatively stable are still very susceptible to deterioration and excavation should be planned accordingly. Excavation of similar shell-midden sites should proceed with the presumption that ceramics of analogous physical and chemical characteristics to the ones studied will exhibit poor preservation. Here it would be useful to prepare separate excavation strategies for ceramics contained within the shell midden and those found in the sandy shell-free soil. This could include supported lifting of large fragments and controlled drying to ensure that substantial fragments were excavated from the shell midden intact. Washing and processing of the materials should also be modified, as abrasion and repeated wetting and drying can exacerbate the already weakened edges of these ceramics. If salt deposits are apparent on the surface of sherds after drying, the assistance of a conservator would be ideal to proceed with the removal of soluble salts and prevent further damage to the ceramic assemblage.

Large ceramics from the dense-shell context should also be provided with additional support in storage, with the presumption that they are subject to damage from handling and pressure from other objects. Many of these sherds have extremely low mechanical strength, and are considerably more fragile than typical ceramics. It would be helpful to inform researchers prior to handling of the fragile nature of the ceramics, so that handling procedures can be established and appropriate precautions taken.

AREAS FOR FUTURE RESEARCH

The small sample size utilized for this study limits in some ways the conclusions that can be reached. It would be useful for future studies to expand the number of ceramics analyzed for a broader or more fine-grained understanding of the conditions occurring in different levels of the site. Comparison with ceramic materials from another shell midden site could also serve to establish the variability of other sites with similar burial environments. Research into different clay and temper types in similar environments could also clarify the degree to which other ceramics are subject to the same differential preservation and deterioration phenomena. The results found here could be further confirmed with x-ray diffraction analysis, on small samples, surfaces, or polished cross-sections. This would help to identify the specific alteration products present and better understand the processes taking place.

The selection of the largest sherds present in a given level can introduce some bias to the results of this study, given that the smallest fragments are often the most deteriorated. While small and heavily deteriorated samples can be challenging to analyze, these samples could give an indication of the outcome of deterioration in highly weakened ceramics. Where possible it would be useful to compare the composition of some of these highly deteriorated pieces.

In particular, this research highlights the need for systemized terminology to assess and describe ceramic deterioration, akin to those typically used in studies of other material types. Detailed schema have been developed for the interpretation of taphonomic processes on faunal material, and the corrosion of metals in burial, and a similarly detailed system for ceramic materials could aid in the interpretation and analysis of assemblages in future research. Future studies could also benefit from in situ testing of the soils, as some error was potentially introduced from testing of

soils some time after they were originally collected.

CONCLUSION

The pronounced differences in ceramic preservation of the Late Archaic fiber-tempered assemblage from St. Catherines Island, GA suggests that the varying burial environments have a significant impact on the deterioration mechanisms and diagenetic processes occurring. The resulting condition of the sherds appears to be closely related to the burial environment. While the results of this research are preliminary, they highlight the issues posed by taphonomic processes for the interpretation of ceramic data. The specific deterioration processes at this site should have a direct impact on the way in which the ceramic data is interpreted. The poor preservation of sherds within a shell midden suggests that the current ceramic distribution is not indicative of the original deposition of materials, and is biased by adverse conditions within the shell deposits. Weathering seems to be more rapid within the dense-shell, and may have resulted in the loss of ceramics buried in the midden. Furthermore, the ceramics within the shell have been subject to the introduction of additional materials and to potential leaching, making comparisons between the chemical composition of the two environments difficult. This highlights the need to consider the burial environments of any site, especially where intra-site variation exists.

Using a combination of non-invasive and invasive analytical techniques, it is possible to obtain valuable data about ceramic composition and deterioration with limited sacrifice of sample materials. Continued research on ceramic deterioration is necessary to understand fully the processes and mechanisms taking place, but this research has aimed to provide a case study in the classification and investigation of ceramic preservation. Fiber-tempered ceramics are a valuable and irreplaceable part of the history of ceramic technology in the United States, and a better understanding of their

condition will assist with future archaeological research, improved excavation strategies, and ensure their continued long-term preservation.

APPENDIX A: VISUAL GLOSSARY

*Terms adapted from Grimmer (1984) and Buys and Oakley (1996).

SURFACE CRACKING

Defined as small fissures of no more than 0.5 cm in width. These cracks are limited to the outer surface of the ceramic sherd, extending no more than 0.5 cm from the exterior.



Figure 22: Surface Cracking

SURFACE DEPOSITS

Defined as accretions or encrustations on the surface of the ceramic, as a result of some external factor. These are typically tightly adhered to the surface, and can include deposits of sand, shell, or other combinations of materials.

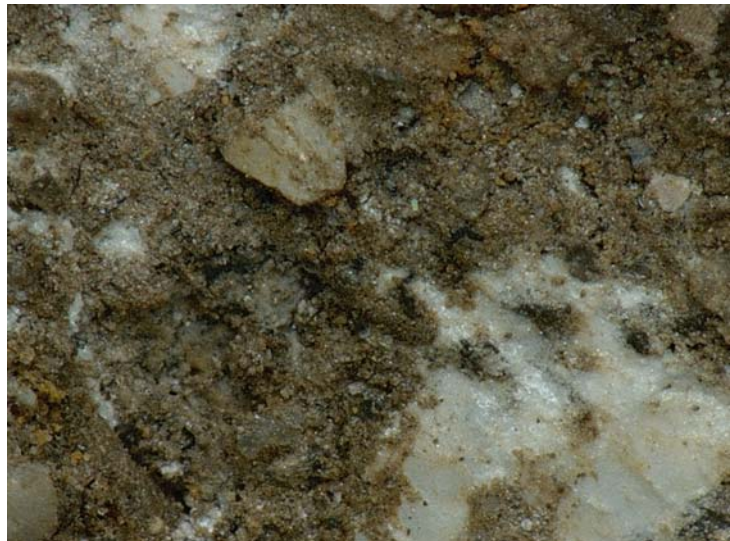


Figure 23: Surface Deposits

GLOSS

A surface with a smooth texture and high level of shine, independent of any surface treatment applied during production of the ceramic.



COLOR ALTERATION

A change in the original color of the ceramic surface, through some interaction with the burial environment or fine deposition of materials on the surface.



EROSION

Wearing away of the surface or edges, through the action of particles or the movement of water in the soil.



Figure 26: Erosion

LOSS

The complete detachment of material from the ceramic, either along the edges or in discrete section of the surface.



Figure 27: Loss

POWDERING

The loss of cohesion to the surface of the ceramic, resulting in a friable texture and easily dislodged grains and sections of material.



Figure 28: Powdering

STRUCTURAL CRACKING

Fissures in the ceramic, no more than 0.5cm wide and extending more than 0.5 cm from the surface, or through the entire width of the ceramic.



Figure 29: Structural Cracking

APPENDIX B: DETAILED METHODOLOGY
SAMPLE SELECTION

N779 E801 – Shell-Free Sandy Soil				
Level	Total number of ceramics recovered	Non-diagnostics over 2.5 cm diameter	Paired Soil Sample?	
2.85-2.755	14	0	Yes	
2.755-2.66	16	1	Yes	
2.66-2.56	19	1	Yes	
2.56-2.46	46	4	Yes	
2.46-2.36	56	8	Yes	
2.36-2.26	18	4	Yes	
2.26-2.16	32	16	Yes	
2.16-2.06	14	5	Yes	
2.06-1.96	6	1	Yes	
1.96-1.86	3	0	Yes	
1.86-1.76	8	5	Yes	
1.76-1.65	6	1	Yes	
1.65-1.56	6	2	Yes	
1.56-1.46	7	3	Yes	
1.46-1.36	12	10	No	
N784 E797 – Dense Shell				
Level	Total number of ceramics recovered	Non-diagnostics over 2.5 cm diameter	Paired Soil Sample?	Dense Shell Deposits?
3.02-2.915	38	5	Yes	No
2.915-2.77	42	11	Yes	Yes
2.77-2.66	68	4	Yes	Yes
2.66-2.60	7	4	Yes	Yes
2.60-2.50	10	8	Yes	Yes
2.50-2.40	6	1	Yes	Yes
2.40-2.31	8	4	Yes	Yes
2.31-2.25	0	0	Yes	No
N784 E811 – Dense Shell				
Level	Total number of ceramics recovered	Non-diagnostics over 2.5 cm diameter	Paired Soil Sample?	Dense Shell Deposits?
2.94-2.84	13	5	Yes	No
2.84-2.74	17	2	Yes	Yes
2.74-2.59	16	1	Yes	Yes
2.59-2.53	4	0	Yes	Yes
2.53-2.42	2	0	Yes	Yes
2.42-2.25	1	0	Yes	Yes
2.25-2.17	0	0	Yes	No

Table 2: Information considered when choosing samples for analysis. The shaded levels were selected for analysis and used in the course of this study.

CLASSIFICATION SCHEME: DETERIORATION PHENOMENA

Deterioration Type	Method of Determination
Surface Deterioration	
Surface Cracking	Severity
Surface Deposits	Severity
Gloss	Presence/Absence
Color Alteration	Presence/Absence
Structural Deterioration	
Erosion	Severity
Loss	Severity
Powdering	Severity
Structural Cracking	Severity

Table 3: Classification approaches for each deterioration type.

- Severity determined by the percentage of the surface affected:
 - None: No indication of the deterioration phenomena present
 - Minor: One-third or less of the total surface
 - Moderate: Between one-third and two-thirds of the total surface
 - Severe: More than two-thirds of the total surface
- Each level was assigned a numerical value, for a possible range of 0 to 20:

SEVERITY		PRESENCE/ABSENCE	
None:	0	Absence:	0
Minor:	1	Presence:	1
Moderate:	2		
Severe:	3		
- The total values for the eight types of deterioration were tallied for each sherd, to give an idea of the overall deterioration, regardless of type. The values, ranging from a possible 0 to 20, were divided into equal parts, to categorize the severity levels:
 - Excellent: 0 – 3
 - Good: 4 – 7
 - Fair: 8 – 11
 - Poor: 12 – 15
 - Failing: 16 – 20

SOIL TESTING PROCEDURES

Based on procedures outlined by Tan (1996), Stein (1984), and Odegaard et al (2000).

Organic Materials and Carbonate Content:

1. Soil was sieved through 2 mm mesh, and air-dried for twenty-four hours. The larger fraction was set aside, and was not used for analysis.
2. Crucibles were heated in a furnace to 1000°C for 30 minutes to remove any residual material on the surface, and weighed to four decimal places on a digital scale.
3. Samples were placed into the cleaned crucibles and desiccated in a drying oven at 90°C for one hour, then transferred to a desiccator and allowed to cool. The weight of the samples was then measured, and recorded as the dry weight.
4. The samples were then placed into a furnace heated to 550°C for one hour. They were then removed from the oven to a desiccator and allowed to cool before weighing again. This weight, when compared to the original dry weight, represents the total loss of organic material in the soil sample.
5. The samples were then placed into a furnace heated to 1000°C for one hour. They were again removed to a desiccator and allowed to cool before weighing. This weight, when compared to the original dry weight, represents evolution of carbon dioxide from the sample, and by proxy, the carbonate content of the sample.

pH Testing:

1. The pH meter was calibrated with buffer solutions of pH 4.0 and pH 7.0.
2. Twenty-five grams of soil were added to a beaker filled with 25 mL of deionized water, and stirred for 15 minutes with a magnetic stir rod.
3. The reading was then immediately taken and recorded as pH value in water.

APPENDIX C: RESULTS OF CONDITION ASSESSMENT

	Catalog #	Unit #	Level (cm below surface)	Group	Depth	Condition
Dense Shell	2846021	N784 E797	10-20	Shell	2.915-2.77	Good
	2846028	N784 E797	10-20	Shell	2.915-2.77	Good
	2846018	N784 E797	10-20	Shell	2.915-2.77	Good
	2846010	N784 E797	10-20	Shell	2.915-2.77	Good
	2846024	N784 E797	10-20	Shell	2.915-2.77	Fair
	2846264	N784 E797	10-20	Shell	2.915-2.77	Fair
	2846014	N784 E797	10-20	Shell	2.915-2.77	Fair
	2846259	N784 E797	10-20	Shell	2.915-2.77	Fair
	2846255	N784 E797	10-20	Shell	2.915-2.77	Fair
	2846009	N784 E797	10-20	Shell	2.915-2.77	Fair
	2846262	N784 E797	10-20	Shell	2.915-2.77	Fair
	2846023	N784 E797	10-20	Shell	2.915-2.77	Poor
	2846263	N784 E797	10-20	Shell	2.915-2.77	Poor
	2846261	N784 E797	10-20	Shell	2.915-2.77	Poor
	2846260	N784 E797	10-20	Shell	2.915-2.77	Poor
	2846025	N784 E797	10-20	Shell	2.915-2.77	Poor
	2846012	N784 E797	10-20	Shell	2.915-2.77	Poor
	2846256	N784 E797	10-20	Shell	2.915-2.77	Failing
	2846564	N784 E797	20-30	Shell	2.77-2.66	Good
	2846565	N784 E797	20-30	Shell	2.77-2.66	Poor
	2846566	N784 E797	20-30	Shell	2.77-2.66	Poor
	2846642	N784 E797	30-40	Shell	2.66-2.60	Fair
	2846301	N784 E797	40-50	Shell	2.60-2.50	Poor
	2846590	N784 E797	60-70	Shell	2.40-2.31	Fair
	2845967	N784 E811	10-20	Shell	2.84-2.74	Good
	2845961	N784 E811	10-20	Shell	2.84-2.74	Fair
	2845965	N784 E811	10-20	Shell	2.84-2.74	Fair
	2845969	N784 E811	10-20	Shell	2.84-2.74	Fair
	2845962	N784 E811	10-20	Shell	2.84-2.74	Poor
	2846054	N784 E811	20-30	Shell	2.74-2.59	Fair

Table 4: Results of condition assessment for ceramics in the dense shell.

	Catalog #	Unit #	Level (cm below surface)	Group	Depth	Condition
Shell-Free	2845291	N779 E801	30-40	Non-Shell	2.56-2.46	Excellent
	2845094	N779 E801	30-40	Non-Shell	2.56-2.46	Excellent
	2845321	N779 E801	30-40	Non-Shell	2.56-2.46	Good
	2845298	N779 E801	40-50	Non-Shell	2.46-2.36	Excellent
	2845156	N779 E801	40-50	Non-Shell	2.46-2.36	Excellent
	2845292	N779 E801	40-50	Non-Shell	2.46-2.36	Excellent
	2845165	N779 E801	40-50	Non-Shell	2.46-2.36	Excellent
	2845181	N779 E801	40-50	Non-Shell	2.46-2.36	Good
	2845155	N779 E801	40-50	Non-Shell	2.46-2.36	Good
	2845295	N779 E801	40-50	Non-Shell	2.46-2.36	Good
	2845153	N779 E801	40-50	Non-Shell	2.46-2.36	Good
	2845296	N779 E801	40-50	Non-Shell	2.46-2.36	Good
	2845392	N779 E801	50-60	Non-Shell	2.36-2.26	Good
	2845319	N779 E801	50-60	Non-Shell	2.36-2.26	Good
	2845393	N779 E801	50-60	Non-Shell	2.36-2.26	Good
	2845371	N779 E801	60-70	Non-Shell	2.26-2.16	Excellent
	2845297	N779 E801	60-70	Non-Shell	2.26-2.16	Excellent
	2845366	N779 E801	60-70	Non-Shell	2.26-2.16	Excellent
	2845372	N779 E801	60-70	Non-Shell	2.26-2.16	Excellent
	2845212	N779 E801	60-70	Non-Shell	2.26-2.16	Excellent
	2845355	N779 E801	60-70	Non-Shell	2.26-2.16	Excellent
	2845299	N779 E801	60-70	Non-Shell	2.26-2.16	Excellent
	2845353	N779 E801	60-70	Non-Shell	2.26-2.16	Good
	2845368	N779 E801	60-70	Non-Shell	2.26-2.16	Fair
	2845309	N779 E801	70-80	Non-Shell	2.16-2.06	Good
	2845326	N779 E801	70-80	Non-Shell	2.16-2.06	Good
	2845306	N779 E801	70-80	Non-Shell	2.16-2.06	Fair
	2845221	N779 E801	100-110	Non-Shell	1.86-1.76	Excellent
	2845220	N779 E801	100-110	Non-Shell	1.86-1.76	Excellent
	2845219	N779 E801	100-110	Non-Shell	1.86-1.76	Good

Table 4 (con.): Results of condition assessment for the ceramics in the shell-free sandy soil.

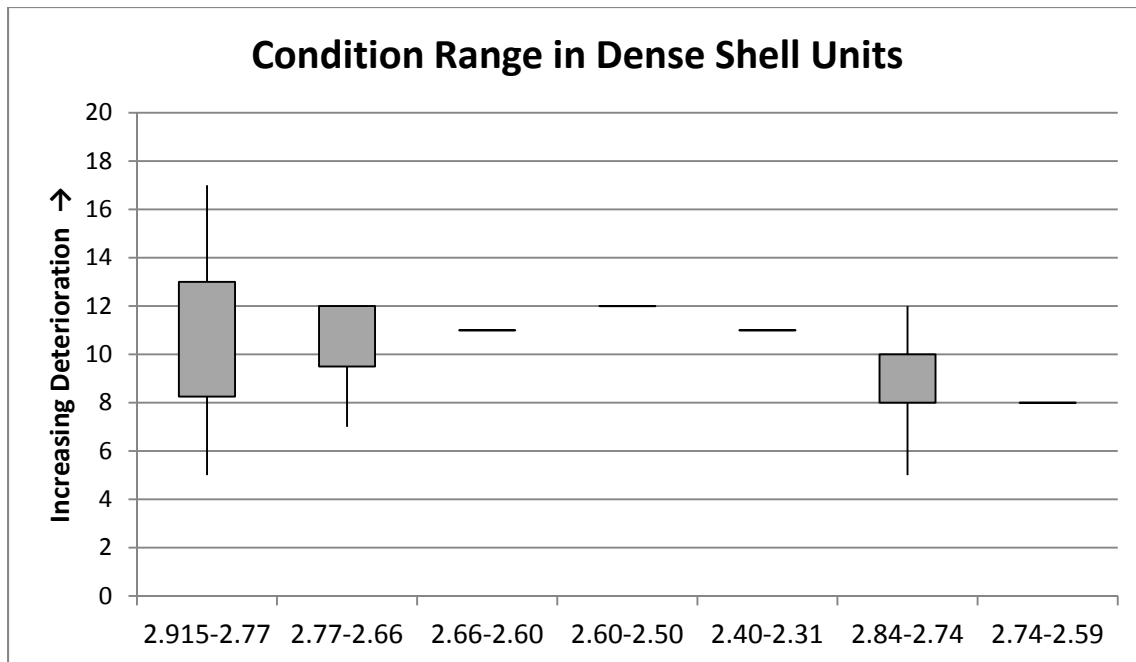


Figure 30: Preservation of ceramic samples in the dense shell, by level.

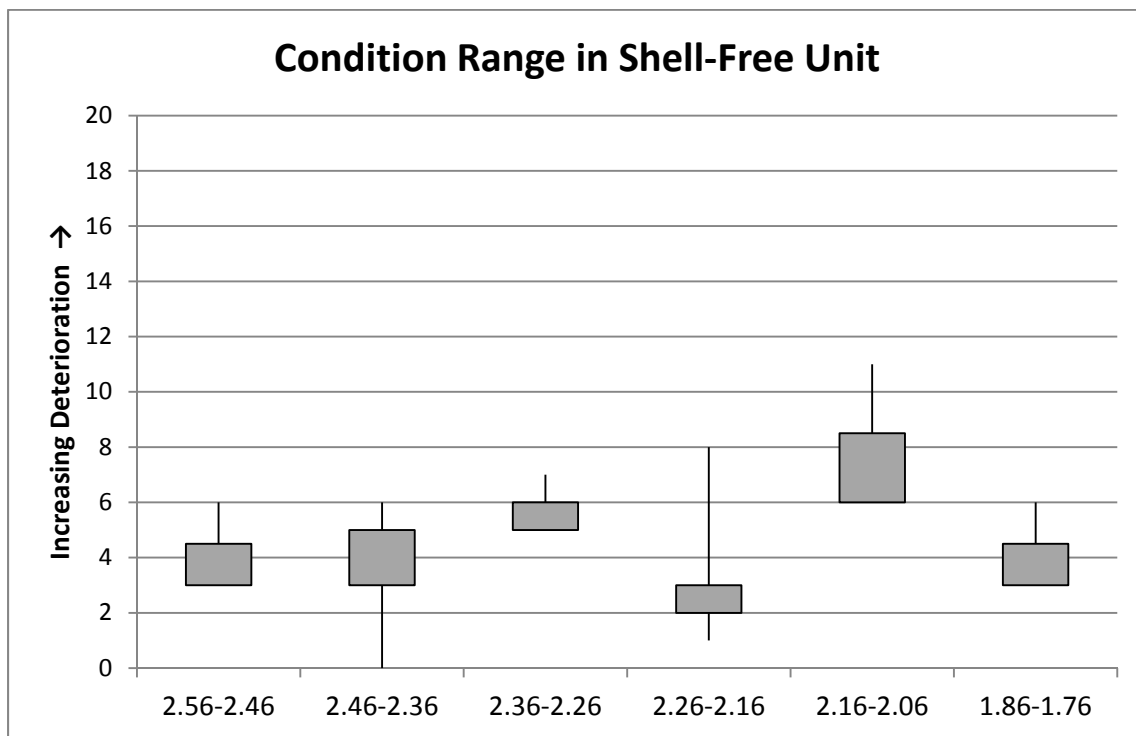


Figure 31: Preservation of ceramic samples in the shell-free area, by level.

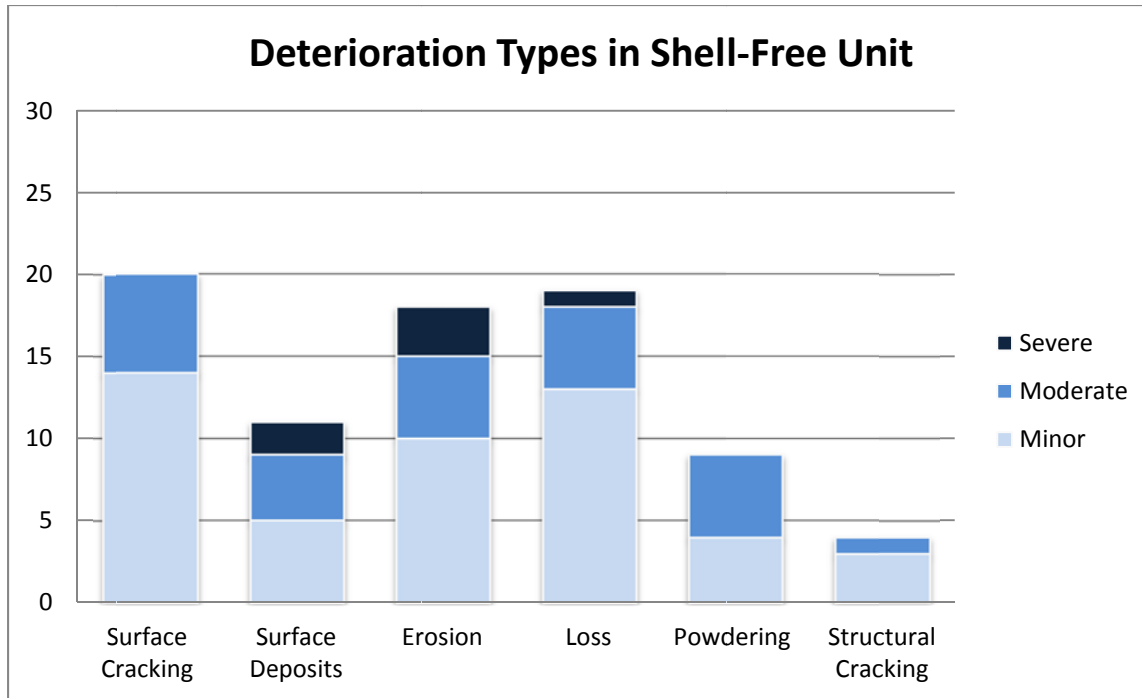


Figure 32: Deterioration in the shell-free area, by type.

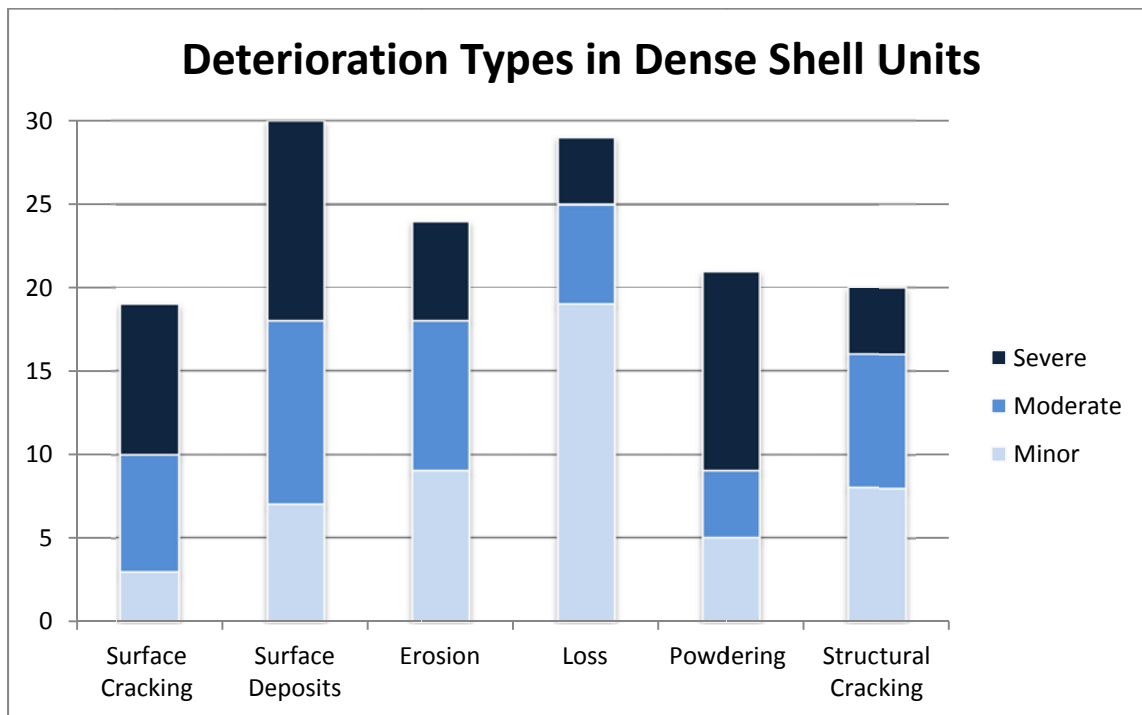


Figure 33: Deterioration in the dense shell, by type.

APPENDIX D: SOIL TESTING RESULTS

	Unit	Level	Weight before testing	Weight after firing at 550°C	Weight (OM)	% Organic Matter (OM)
Dense Shell	N784 E797	2.915-2.77	4.893	4.5667	0.3263	6.669%
	N784 E797	2.77-2.66	4.9237	4.7011	0.2226	4.521%
	N784 E797	2.66-2.60	4.9049	4.6313	0.2736	5.578%
	N784 E797	2.60-2.50	4.9462	4.6642	0.282	5.701%
	N784 E797	2.40-2.31	4.9287	4.7739	0.1548	3.141%
	N784 E811	2.84-2.74	4.85	4.4043	0.4457	9.190%
N784 E811	2.74-2.59	4.8753	4.576	0.2993	6.139%	
Shell-Free	N779 E801	2.56-2.46	4.9482	4.8157	0.1325	2.678%
	N779 E801	2.46-2.36	4.9509	4.8378	0.1131	2.284%
	N779 E801	2.36-2.26	4.9507	4.8492	0.1015	2.050%
	N779 E801	2.26-2.16	4.9653	4.8572	0.1081	2.177%
	N779 E801	2.16-2.06	4.968	4.8553	0.1127	2.269%
	N779 E801	1.86-1.76	4.9738	4.8963	0.0775	1.558%

Table 5: Results, Organic Content in Soil Samples

	Unit	Level	Weight before testing	Weight after firing at 1000°C	Weight (CO ₂)	% Calcium Carbonate
Dense Shell	N784 E797	2.915-2.77	4.5667	3.8177	0.749	34.790%
	N784 E797	2.77-2.66	4.7011	4.0726	0.6285	29.011%
	N784 E797	2.66-2.60	4.6313	4.0545	0.5768	26.727%
	N784 E797	2.60-2.50	4.6642	4.078	0.5862	26.935%
	N784 E797	2.40-2.31	4.7739	4.3588	0.4151	19.141%
	N784 E811	2.84-2.74	4.4043	3.7377	0.6666	31.237%
N784 E811	2.74-2.59	4.576	3.9535	0.6225	29.019%	
Shell-Free	N779 E801	2.56-2.46	4.8157	4.7969	0.0188	0.863%
	N779 E801	2.46-2.36	4.8378	4.8235	0.0143	0.656%
	N779 E801	2.36-2.26	4.8492	4.8259	0.0233	1.070%
	N779 E801	2.26-2.16	4.8572	4.8404	0.0168	0.769%
	N779 E801	2.16-2.06	4.8553	4.8391	0.0162	0.741%
	N779 E801	1.86-1.76	4.8963	4.8803	0.016	0.731%

Table 6: Results, Evolved Carbon Dioxide, and Calcium Carbonate by Proxy

	Unit	Level	pH in water	pH Classification
Dense Shell	N784 E797	2.915-2.77	7.9	Moderately Alkaline
	N784 E797	2.77-2.66	8.1	Moderately Alkaline
	N784 E797	2.66-2.60	8.2	Moderately Alkaline
	N784 E797	2.60-2.50	8.1	Moderately Alkaline
	N784 E797	2.40-2.31	8.3	Moderately Alkaline
	N784 E811	2.84-2.74	8.0	Moderately Alkaline
	N784 E811	2.74-2.59	8.1	Moderately Alkaline
Shell-Free	N779 E801	2.56-2.46	7.3	Neutral
	N779 E801	2.46-2.36	7.5	Slightly Alkaline
	N779 E801	2.36-2.26	7.3	Neutral
	N779 E801	2.26-2.16	7.3	Neutral
	N779 E801	2.16-2.06	7.4	Slightly Alkaline
	N779 E801	1.86-1.76	7.1	Neutral

Table 7: pH Values, by Level. Classifications derived from USDA (1998).

	Unit	Level	Conductivity	k_{adj}
Dense Shell	N784 E797	2.915-2.77	252	0.252
	N784 E797	2.77-2.66	148	0.148
	N784 E797	2.66-2.60	149	0.149
	N784 E797	2.60-2.50	167	0.167
	N784 E797	2.40-2.31	160	0.16
	N784 E811	2.84-2.74	229	0.229
	N784 E811	2.74-2.59	163	0.163
Shell-Free	N779 E801	2.56-2.46	88	0.088
	N779 E801	2.46-2.36	93	0.093
	N779 E801	2.36-2.26	51	0.051
	N779 E801	2.26-2.16	67	0.067
	N779 E801	2.16-2.06	73	0.073
	N779 E801	1.86-1.76	133	0.133

Table 8: Conductivity Readings, by Level

	Unit	Level	Carbonates (CO ₃)	Sulfates (SO ₄)	Nitrates (NO ₃)	Chlorides (Cl)
Dense Shell	N784 E797	2.915-2.77	Positive	Negative	Positive	Negative
	N784 E797	2.77-2.66	Positive	Negative	Positive	Negative
	N784 E797	2.66-2.60	Positive	Negative	Positive	Negative
	N784 E797	2.60-2.50	Positive	Negative	Positive	Negative
	N784 E797	2.40-2.31	Positive	Negative	Positive	Negative
	N784 E811	2.84-2.74	Positive	Negative	Positive	Negative
	N784 E811	2.74-2.59	Positive	Negative	Positive	Negative
Shell-Free	N779 E801	2.56-2.46	Negative	Negative	Positive	Negative
	N779 E801	2.46-2.36	Negative	Negative	Positive	Negative
	N779 E801	2.36-2.26	Negative	Negative	Positive	Negative
	N779 E801	2.26-2.16	Negative	Negative	Positive	Negative
	N779 E801	2.16-2.06	Negative	Negative	Positive	Negative
	N779 E801	1.86-1.76	Negative	Negative	Positive	Negative

Table 9: Results of microchemical tests for salt species.

Microchemical tests are taken from Odegaard et al (2000) . The test description and limits of detection (where known) are listed below:

- **Carbonates:** Test for carbonate using hydrochloric acid and barium hydroxide
- **Sulfates:** Test for sulfate using barium chloride
Sensitive to 50-70 ppm sodium sulfate
- **Nitrates:** Test for nitrate using iron (II) sulfate
Sensitive to 1% w/v and above
- **Chlorides:** Tests for chloride using silver nitrate

APPENDIX E: PORTABLE X-RAY FLUORESCENCE RESULTS

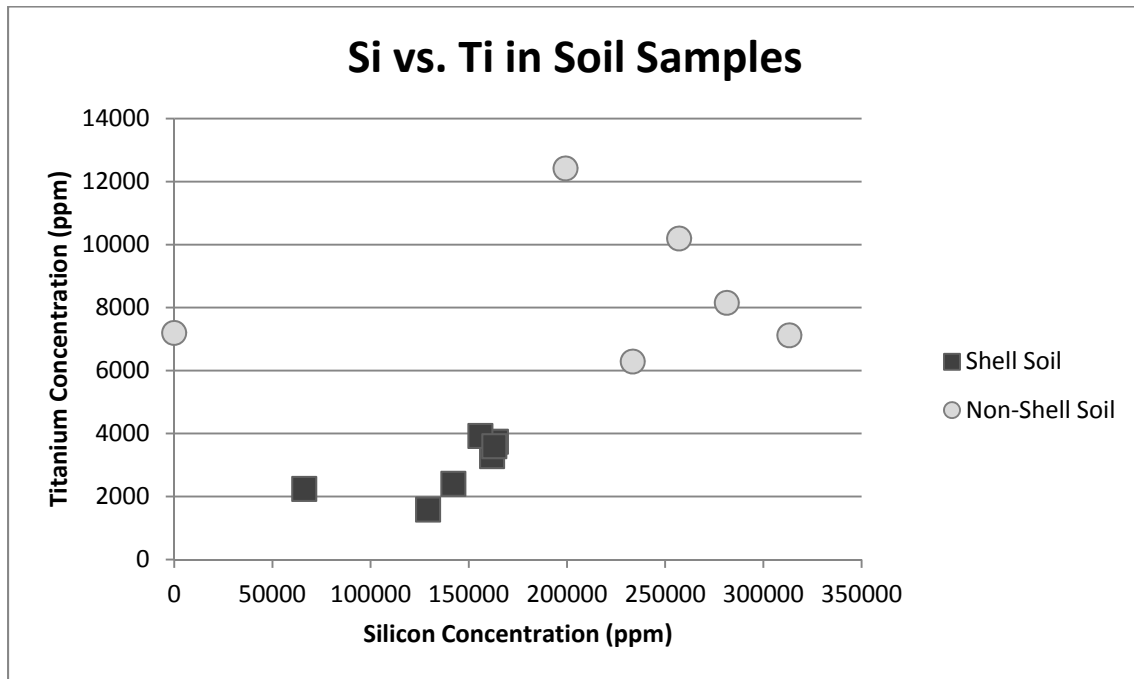
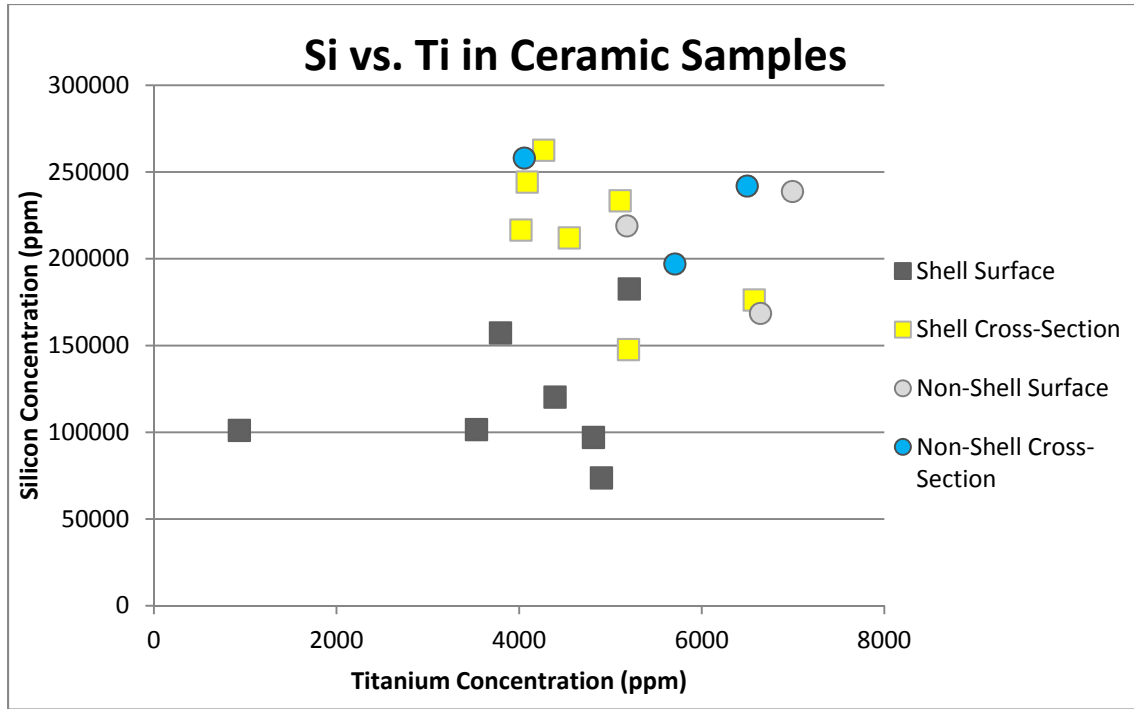


Figure 34: Silicon and titanium ratios in the Niton pXRF results.

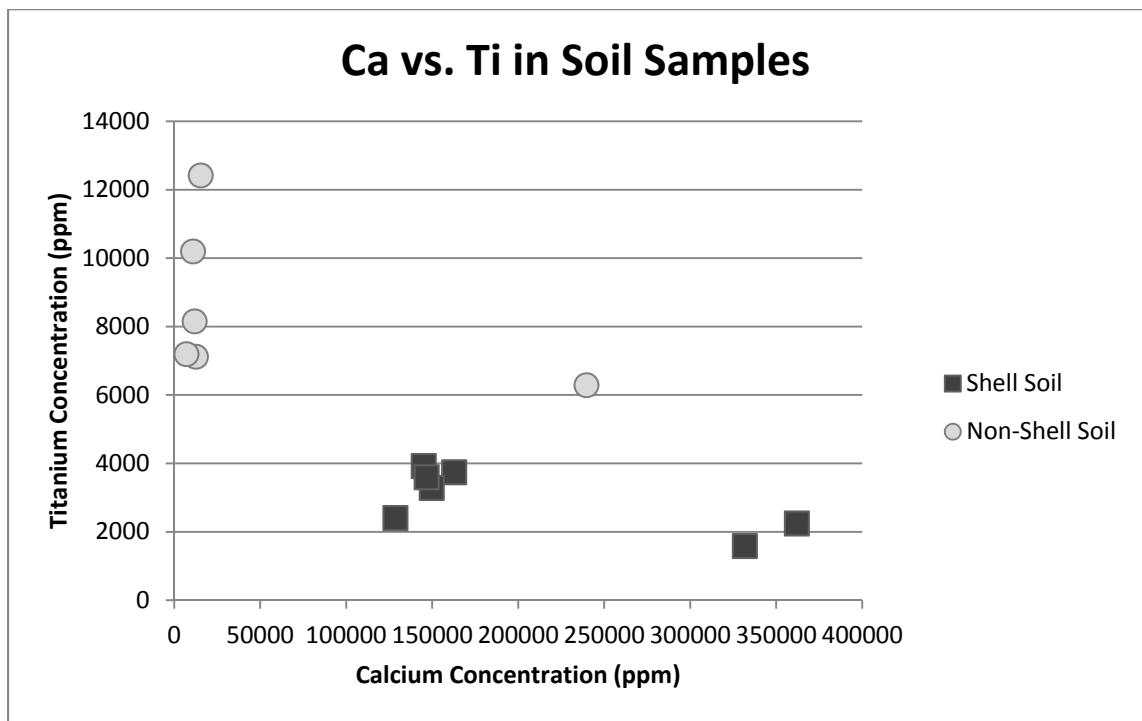
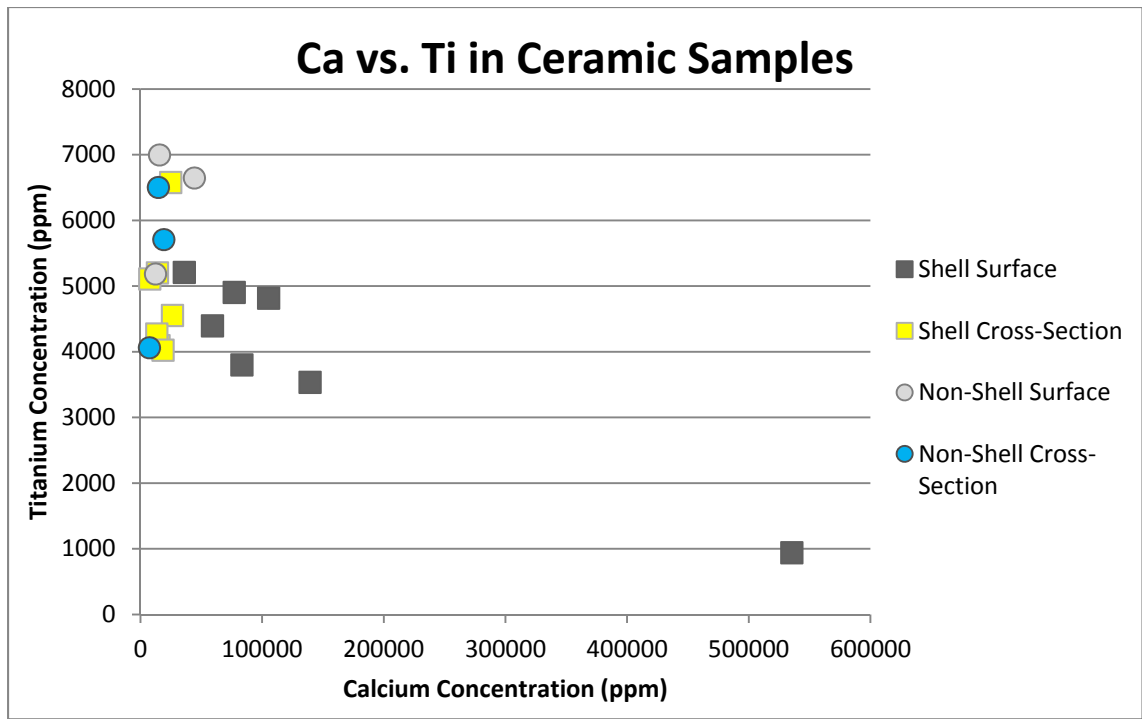


Figure 35: Calcium and titanium ratios in the Niton pXRF results.

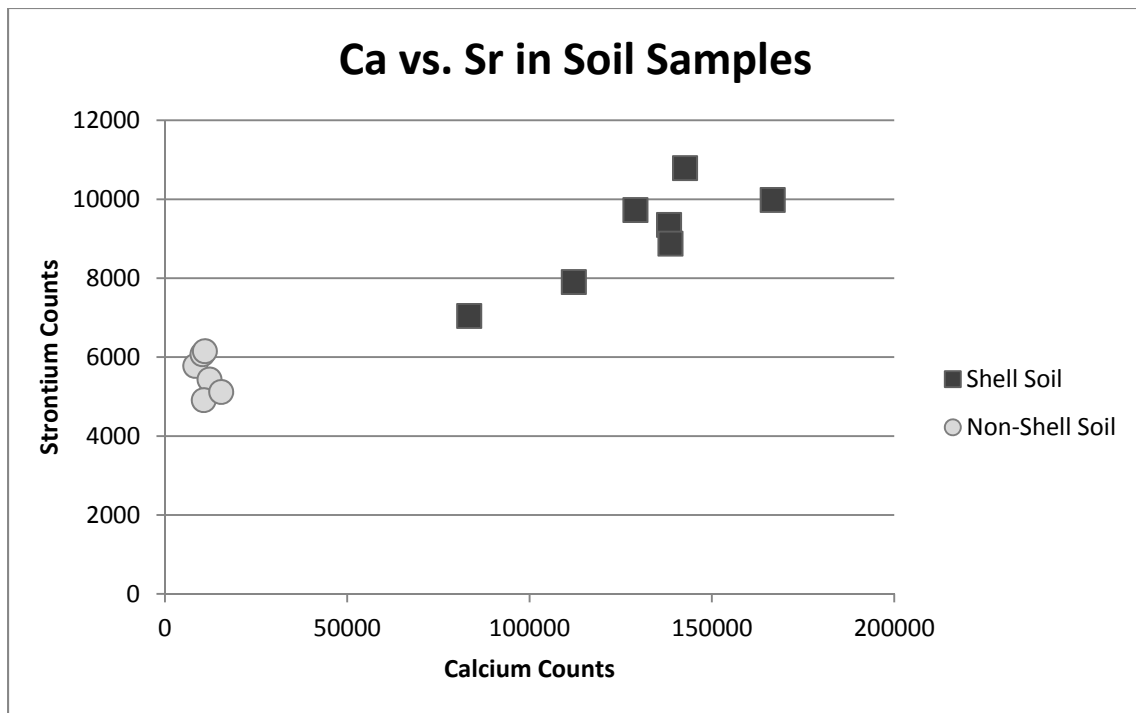
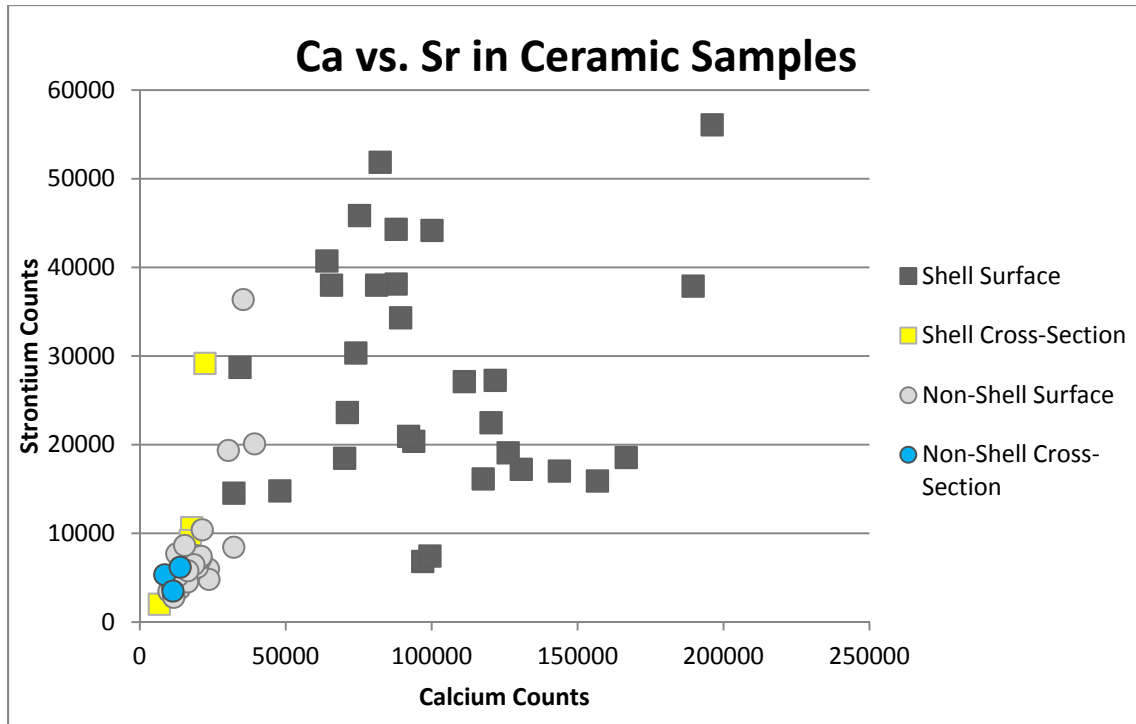


Figure 36: Calcium and strontium ratios in the Bruker pXRF results.

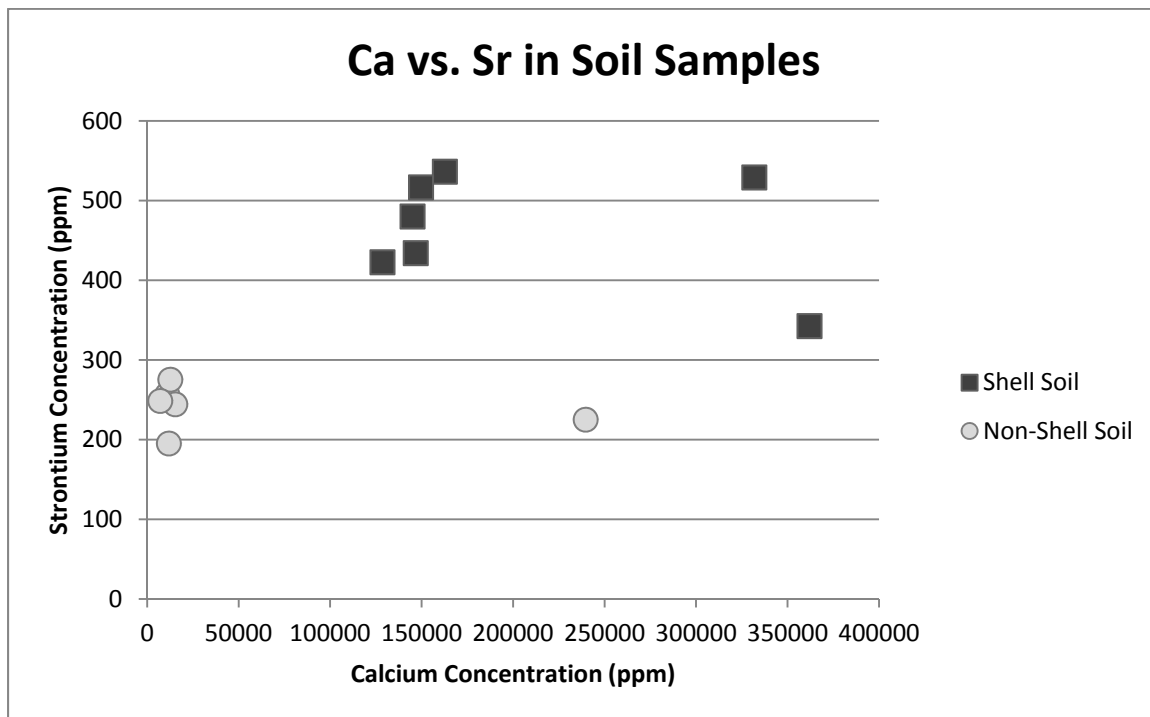
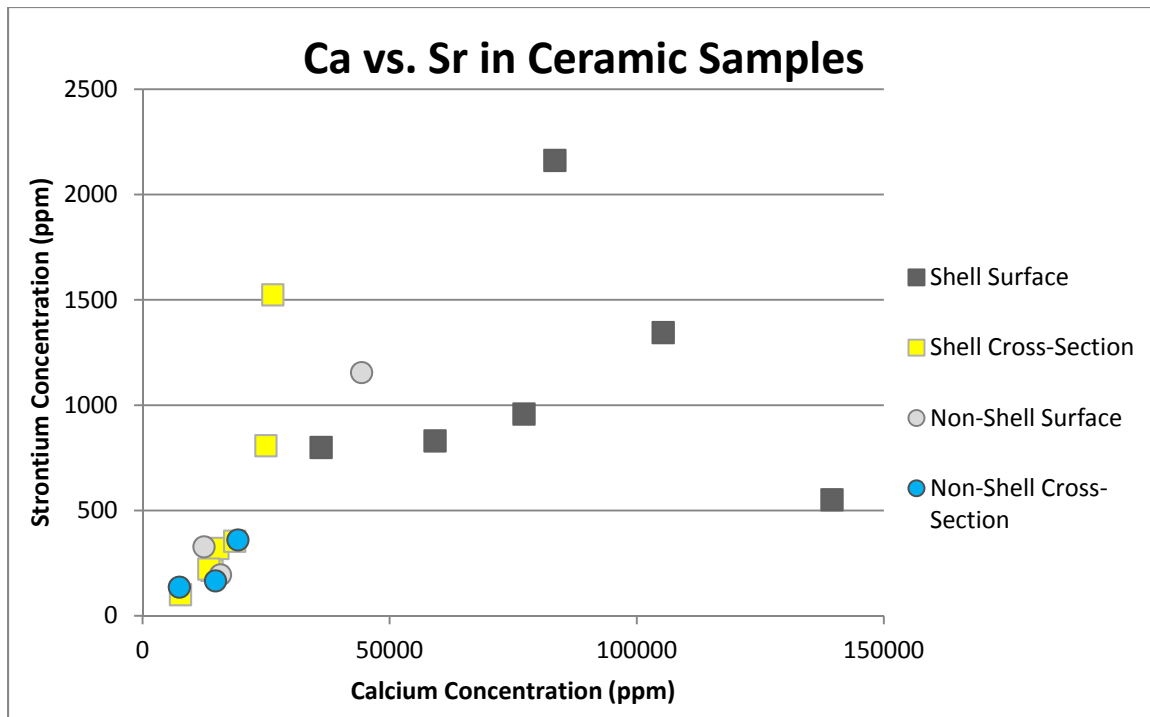


Figure 37: Calcium and strontium ratios in the Niton pXRF results.

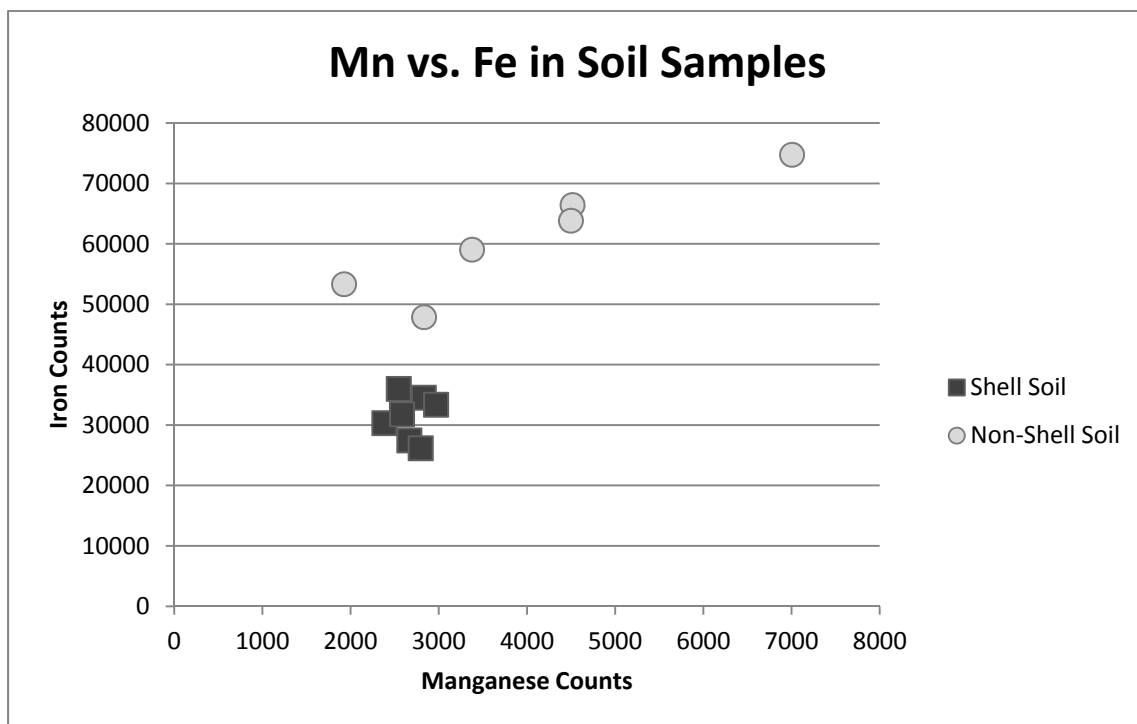
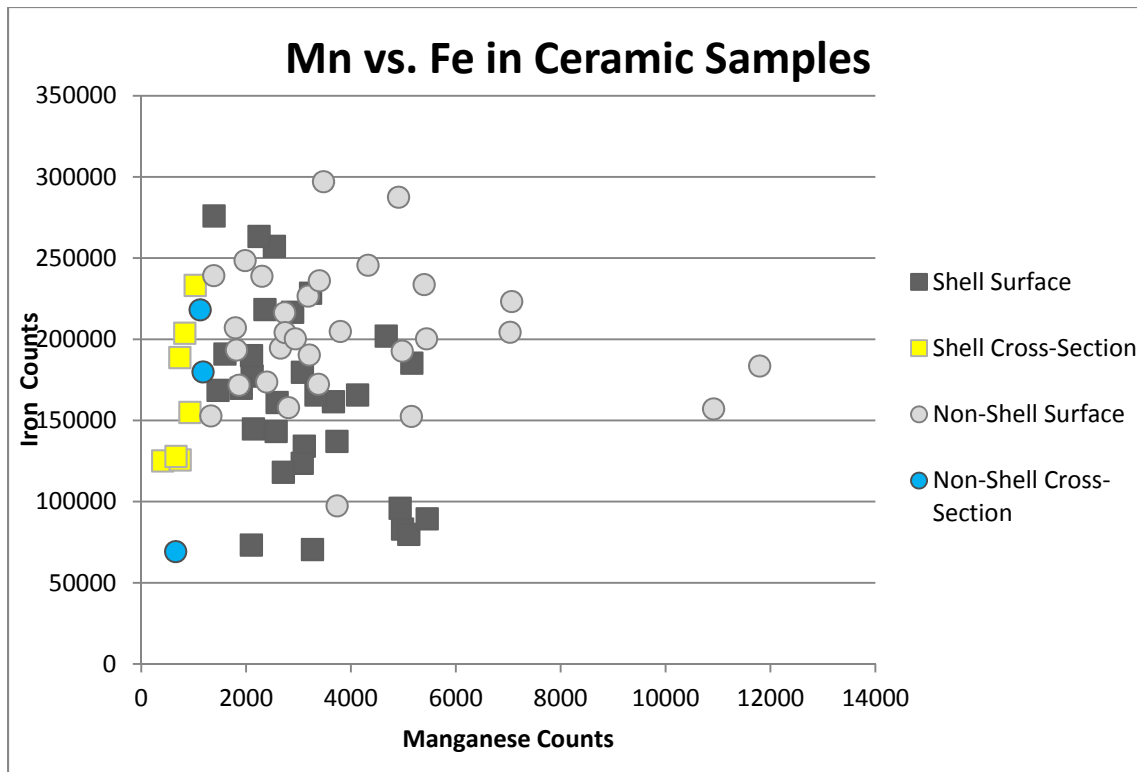


Figure 38: Manganese and iron ratios in the Bruker pXRF results.

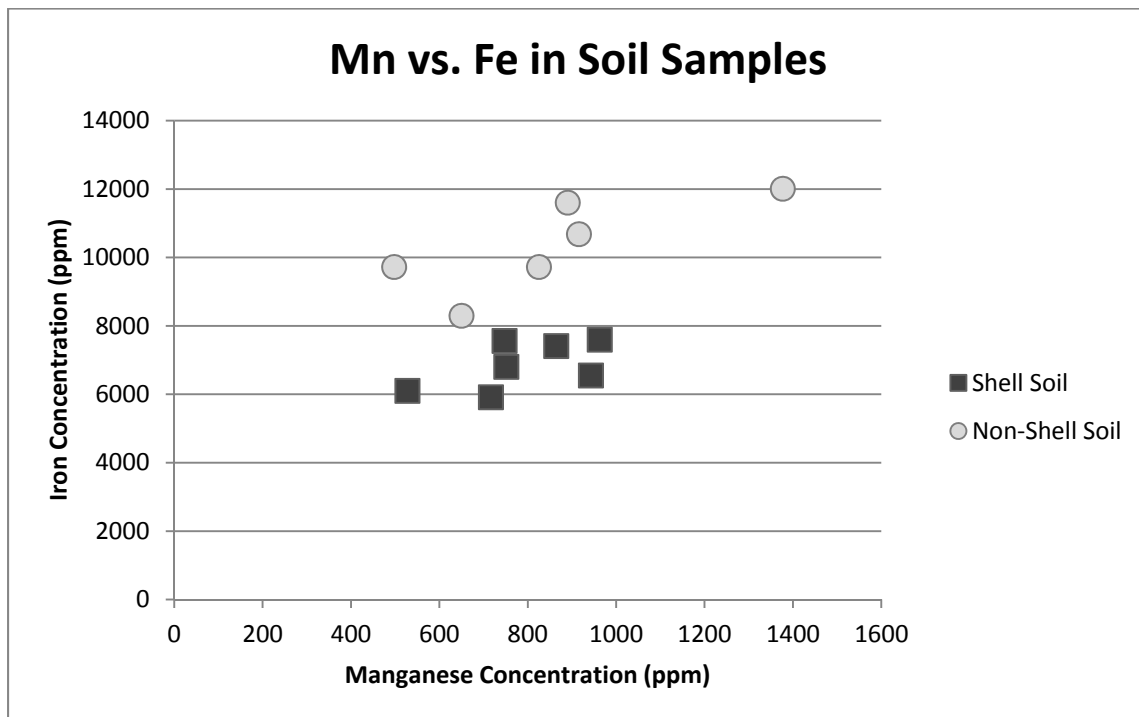
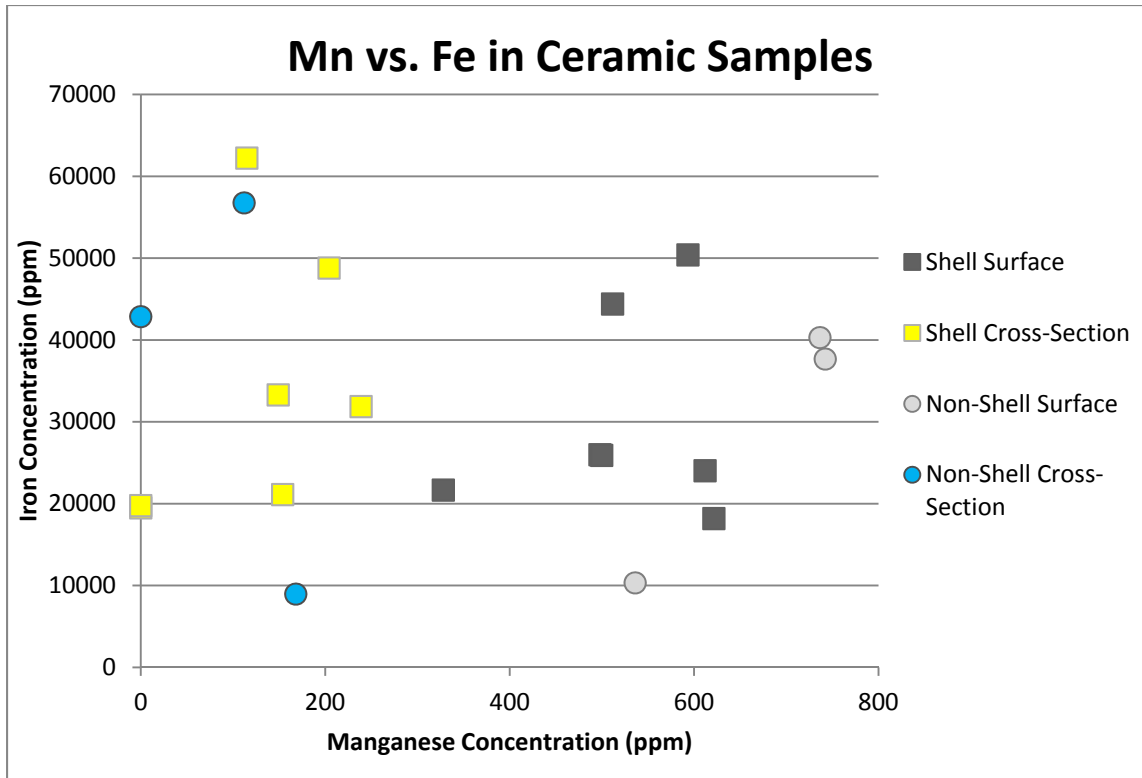


Figure 39: Manganese and iron ratios in the Niton pXRF results.

APPENDIX F: VARIABLE PRESSURE SCANNING ELECTRON MICROSCOPY RESULTS

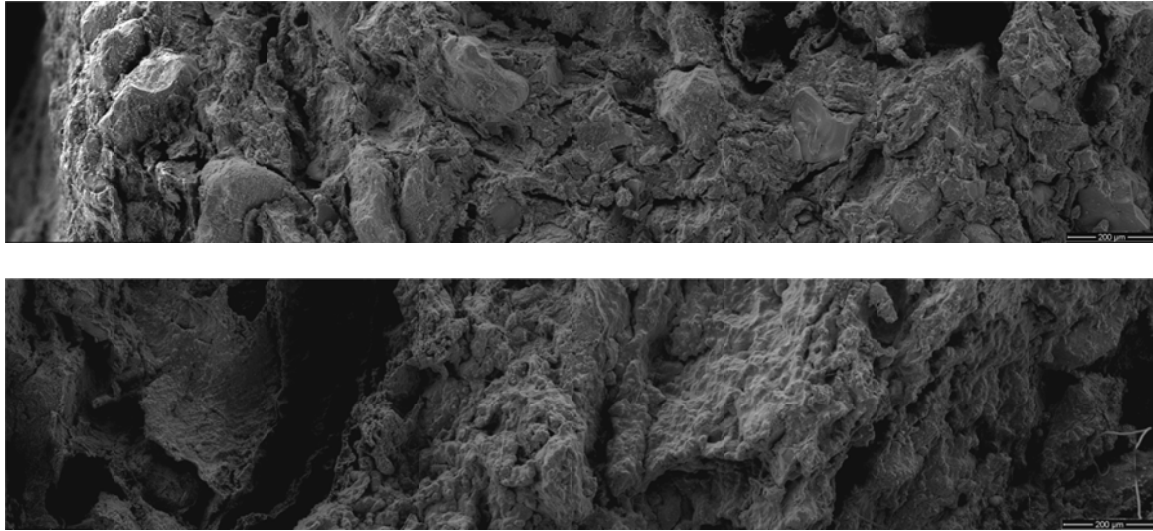


Figure 40: Composite images of the cross-section of sample 28.4/6018, taken with the low-vacuum detector (LVD) at 200x magnification.

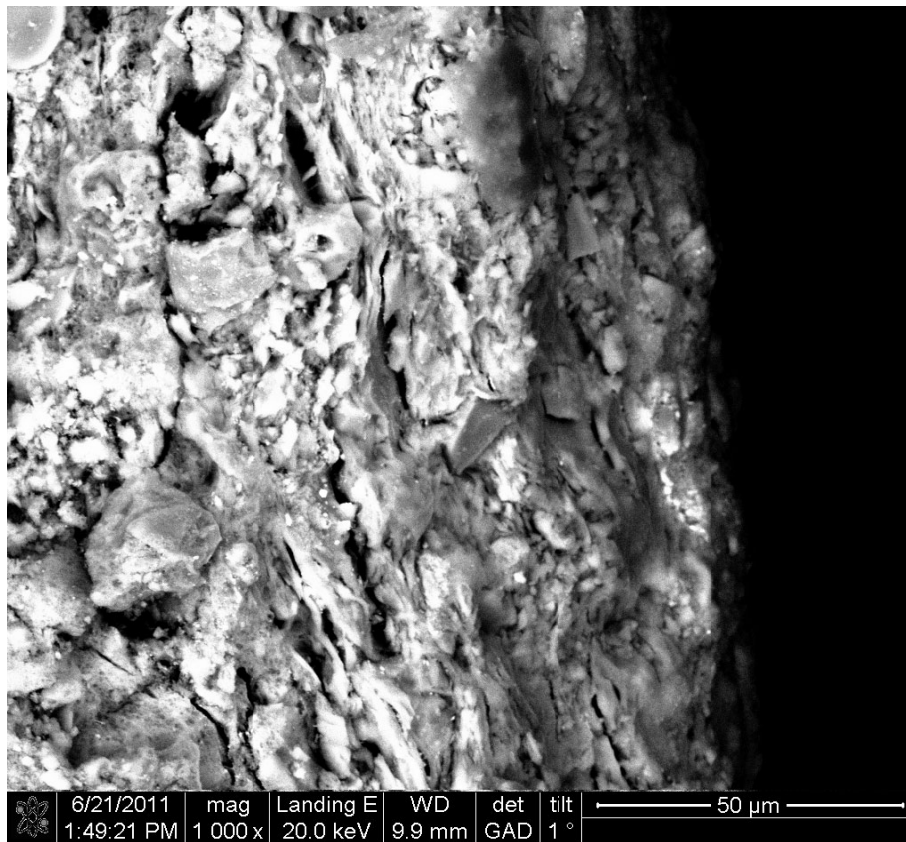


Figure 41: Backscatter electron image of sherd #28.4/6642, corresponding to the EDS results shown in Figure 9.

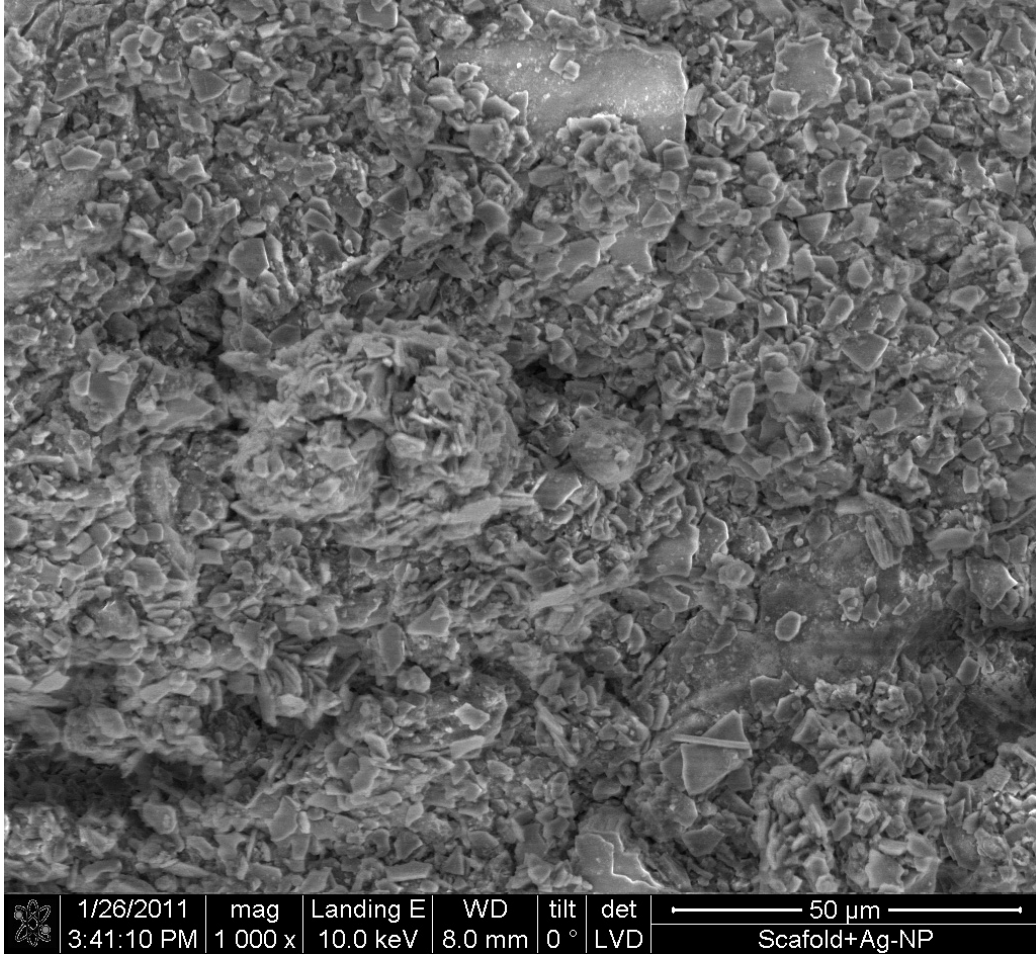


Figure 42: Secondary electron image of sherd #28.4/6021, showing the fine deposition of materials on the surface.

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