Beyond Sourcing: portable X-ray fluorescence and archaeological ceramics

by

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Abstract

Handheld portable X-ray fluorescence (pXRF) technology has been increasingly employed in ceramic provenance studies. While these applications have been largely successful, the utility of this technology for ceramic analysis has nonetheless been called into question. This thesis considers the utility of pXRF for the analysis of archaeological ceramics. It is argued that the analysis of ceramics using any geochemical technique must recognize and account for the range of environmental and technological factors that influence ceramic composition. Ceramics are synthetic and heterogeneous, and thus present a special set of challenges for analysis using non-destructive techniques such as pXRF. Variability in pXRF analysis is assessed in this thesis at both the level of the individual artifact, and at the level of the assemblage.

Archaeological ceramics from sites in Fiji, Tonga, and Jamaica are analyzed using pXRF to assess analytical variability from the perspective of “repeatability”. Substantial variability is evident in the results of repeat, sequential measurements of individual ceramic sherds. In particular, consistent differences are observed between the “core” and “surface” of the sherds. Variability generally increases when larger temper grains are present in the paste matrix. Analytical variability, therefore, appears to relate to both the compositional properties of ceramics, as well the known parameters of non-destructive pXRF analysis. A case study using pXRF to characterize an expanded sample of Fijian ceramics demonstrates the efficacy of a geochemical inventory strategy for identifying compositional differences within and between assemblages.

This thesis highlights the need for independent theory and protocol governing non-destructive analysis of ceramics. The unique capabilities of pXRF are best exploited when the physical properties of specimens and the analytical parameters of the technique are critically examined in tandem. That pXRF analysis “averages” the geochemistry of the ceramic paste constituents is, in light of this broader understanding of ceramic composition, actually advantageous.

Keywords: Ceramic geochemistry; portable X-ray fluorescence (pXRF); analytical repeatability; ceramic technology; geochemical inventory; Fijian ceramics
To my Dad, who took us fossil hunting, and sparked my interest in the past.
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Chapter 1: Introduction

Ceramic geochemistry is a rapidly developing field of archaeological science, one in which technological advances continually expand the research potential of clay and temper provenance studies. Approaches to ceramic compositional analyses are diverse, and are a direct reflection of the diversity of archaeological ceramics themselves (Whitbread 2001); archaeometrists deal with everything from the composition of low-fired earthenwares to glaze recipes on historic and industrial tradewares. The technological choices made by archaeologists depend, to a degree, on the technological choices made by potters in the past – although they are also influenced greatly by research design and feasibility. The decision to employ, for example, X-ray fluorescence over neutron activation analysis is one that is embedded in the nature of the research, the types of questions being asked, and the character of the material itself.

This thesis is concerned with one technological strategy for ceramic compositional analysis: portable X-ray fluorescence (pXRF). Portable and handheld-portable geochemical analyzers are currently becoming popular in archaeology, owing to their capacity for rapid, in situ analysis. Several recent studies have evaluated the utility of pXRF for analysis of archaeological materials, most notably for use with obsidians (Craig et al. 2007; Millhauser et al. 2011; Nazaroff 2010; Phillips and Speakman 2009; Sheppard et al. 2010). Other evaluative studies have focused on pXRF and ceramics (Forster et al. 2011; Goren et al. 2010; Romano et al. 2006), and still others on broader comparisons of PXRF and other geochemical techniques, as well as inter-instrument performance (e.g. Goodale et al. 2012). While these studies generally find good internal
consistency in results from pXRF, they sometimes find “accuracy” lacking, making
integration with absolute data generated by other techniques difficult. Consensus is still
distant on the role of pXRF in provenance studies, especially for use with heterogeneous
geological materials. The goal of this thesis research, therefore, is to investigate the
utility of pXRF for compositional analysis of low-fired earthenware ceramics, one of the
most abundant archaeological materials on the planet. This is accomplished through a
series of controlled experiments on archaeological pottery specimens from assemblages
in the South Pacific and the Caribbean. The experimental design demonstrates the
special capabilities and drawbacks of this technique, based on an understanding of
pottery as a complex, synthetic technology. This thesis considers a research strategy
that investigates compositional variability in archaeological ceramics on multiple levels.

This introductory chapter provides context for study of ceramics in archaeology,
including a case study illustrating a multi-pronged approach to ceramic analysis. This is
followed by a more pointed discussion of the goals and strategies of ceramic
geochemistry. The chapter concludes with an outline of the structure of the thesis.

**Context: ceramics in archaeology**

Archaeologists have long been interested in past migrations, culture contact, and
sustained long-distance interactions between disparate groups. Indeed, for much of the
discipline’s formative development, culture change was explained almost exclusively in
terms of migration and diffusion (e.g., Childe 1958). While intellectual priorities have
shifted considerably in recent decades, material evidence for the movement of people,
objects, and ideas remains at the forefront of discussions and debates on the nature of
societal variation across space and through time. Objects, created in one place,
transported by past agents, and deposited in distant or exotic contexts, form the basis of most, if not all, culture-historical narratives. Not surprisingly, archaeologists have devoted considerable time and effort to the physical demonstration of these processes. The archaeological community has a long tradition of methodological development in the realm of exploring artifact provenance, a tradition often influenced by developments in the physical and chemical sciences. Ceramics are among the most common artifacts to be investigated for compositional properties that divulge their provenance.

Ceramics are among the most widespread classes of artifacts in the world, manufactured on every continent at different times in history. The use of pottery began deep in the past and continues to flourish in communities around the world today. As Lambert (2005:487) suggests, “Human beings became chemists when they began to transform matter purposefully from one chemical form to another” – thus pottery making, which involves the intentional application of heat to carefully mixed raw ingredients, can be considered one of humankind’s oldest and most successful chemistry experiments. Pottery has served a multitude of functions, from utilitarian roles in food preparation and storage, to playing roles in high art, ritual and religion, and economic exchange. Archaeologists for decades have relied on pottery to learn about subsistence, technology, chronology, and trade in past societies (Orton et al. 1996). Chief among the traditional archaeological uses of pottery has been the analysis of stylistic attributes to build cultural chronologies and explore processes of diffusion and migration in the past. This tradition of research began with Flinders Petrie’s ceramic seriation in the Egyptian desert in the 19th century (Trigger 2006:200), and continues to this day (e.g., Peeples and Schachner 2012).
A second avenue of archaeological investigation using ceramics, and the primary focus of this thesis project, has focused on physico-chemical approaches to characterizing and sourcing the raw materials used in pottery production. A variety of techniques borrowed from the physical sciences have been utilized to examine technological aspects of ceramics, their role in prehistoric economies, and their geographical distribution. Just as obsidians and fine-grained lithic materials are routinely traced to their geological origins (e.g., Shackley 1998a), efforts are now made to understand the geographic and cultural origins of ceramics and their constituent ingredients. Because they represent a complex admixing process, ceramics are enormously informative about decision-making and human-environment interactions (Whitbread 2001). Whitbread credits Matson (1965) as the innovator behind the term “ceramic ecology” – a holistic approach to pottery concerned with materials availability, technological processes, and role of the finished product in the culture of the artisan.

Perhaps nowhere have the various and complementary approaches to ceramic analysis been combined so fruitfully as in the archaeology of exploration and settlement in the South Pacific. These analyses are described below in a representative illustration.

**Lapita dispersals: complementary approaches in ceramic analysis**

Archaeologists working in South Pacific routinely use chemical, mineralogical, and stylistic analyses to explore migrations and trade between island societies in the past. This case study illustrates the research potential of integrated, multi-pronged approaches to ceramic analysis.
The South Pacific is a vast region comprising of thousands of islands, from extensive volcanic archipelagoes to remote, low-lying coral atolls. Human occupation of these islands began in the Pleistocene, with initial hunter-gatherer colonization of islands off the northeast coast of New Guinea and the Solomon Islands as early as 35,000 - 40,000 years BP. Pottery appearance in this region around 3500 BP signals the beginning of one of the largest dispersals of a linguistic family in the history of humankind (Kirch 2000). These Austronesian-speaking horticulturalists began their spread eastward in island Southeast Asia, and by 2800 BP their descendants had occupied the major South Pacific archipelagoes up to and including Samoa. Exploration and settlement required some of the longest open-ocean voyaging events in history; a crossing of over 850 km separates Vanuatu from the Fiji Islands, a feat accomplished by colonizing groups of “Lapita” peoples by at least 3050 BP (Nunn 2007).

The various and complementary approaches to ceramic analysis have been vital in tracking these migrations from island to island have. The Lapita produced an elaborate and distinctive suite of ceramic vessels, leaving behind evidence of their stylistic and technological systems. The nature and timing of colonization events throughout the Lapita dispersal region, as well as subsequent processes of isolation and/or interaction (e.g., Burley and Connaughton 2010; Chiu 2007; Clark and Murray 2006; Sand 2000; Summerhayes 2000) have been studied using stylistic changes through time. Though inter-island transfer of ceramics was limited, mineralogical and chemical analyses of ceramic pastes and tempers inform discussions of voyaging, interaction, and technological change (e.g., Burley and Dickinson 2001, 2010; Dickinson 2006; Green 1996; Kennett et al. 2004).
Nukuleka is the site of the earliest known Lapita settlement in Tonga, situated on the Fanga ‘Uta lagoon of Tongatapu, the largest island in the archipelago. The site was first investigated in 1964, and was revisited by a team led by David Burley beginning in 1999 (Burley and Dickinson 2001, 2010; Burley et al. 2010). In making an argument for the recognition of Nukuleka as Tonga’s “founding settlement”, the investigators drew on three lines of evidence based on the abundant ceramics that occur at the site: design elements, geochemistry, and petrography/mineralogy.

Tonga is one of the last archipelagoes to have been settled by Lapita explorers, several centuries after their initial dispersal out of the Bismarck Archipelago in the west. As such, Lapita ceramic design elements found in the majority of Tongan sites reflect an “eastern” design province, with simplified versions of elaborate western motifs resulting in part from a time-decay process (Clark and Murray 2006), in addition to founder effect (Burley and Dickinson 2010). Investigations at Nukuleka, however, revealed the presence of characteristically “western” design elements, suggestive of a colonizing event by people more closely descended from earlier, western Lapita populations. Stylistic analysis thus contributed one line of evidence for Nukuleka’s standing as Tonga’s earliest site.

Complementary analyses based on the mineralogy and chemistry of the Nukuleka ceramics supported this argument. A small portion of the ceramic assemblage was composed of visually distinctive “tan” coloured sherds – contrasting starkly with the majority of red paste ceramics found in other pottery-bearing sites on the Tongan archipelago. Geochemical analysis (Burley and Dickinson 2010), using a handheld portable X-ray fluorescence device, indicated that the handful of tan paste sherds formed a distinct chemical compositional group, making their visible differences
empirically demonstrable and posing the obvious question: why are they different? In addition to this, the chemical profiles of the sherds indicated higher relative levels of K, Ca, Ti, Cr, and Zr, which, taken together, are suggestive of a different geology than occurs in the Tongan island group. The geochemistry also indicated source origin homogeneity, meaning that all the tan paste sherds likely came from the same place.

Petrographic analysis, which attempts to identify the individual minerals present in the ceramic pastes, revealed the presence of temper grain minerals that could not have originated anywhere in Tonga or the adjacent island groups of Samoa or Fiji (Burley and Dickinson 2010). These authors suggest a geological origin far to the west, a suggestion that, if validated, would have profound implications for the nature of Lapita exploration and settlement in the southwestern Pacific region.

The case of the anomalous sherds of Nukuleka serves to illustrate the potential of a multi-pronged approach to ceramic analysis, one that highlights the unique capabilities of each technique, but also their reliance on other techniques for support. Geochemistry, in this case, served to further investigate what was, to the naked eye, already obvious – that these tan paste sherds were unique among the pottery of Tonga. XRF analysis revealed the empirical basis for what was already noticeable to the naked eye. It’s easy to imagine a similar scenario, but one in which there were no obvious visual characteristics that separated one group of ceramic sherds from another (e.g., all of them are red). Establishing the chemical profiles of a large sample of sherds from the assemblage would likely identify the presence of separate compositional groups, groups that could then be sub-sampled and investigated further. The meaning behind these separate groups is, of course, a difficult issue. Are they different because they were transported from another geological region, or did the potters simply combine different
types or amounts of locally-available raw ingredients? Did the pots have a different purpose during their use-life, one that might impact their chemical makeup? Do the different compositional groups reflect differential preservation, with one group the result of post-depositional weathering or chemical leaching? These are questions that can be answered using different experimental approaches, described in more detail below.

In a recent comment piece in *Archaeometry*, Hector Neff (2012) refuted what he calls an “absolutist” perspective of the superiority of mineralogy to chemistry-based ceramic provenance research – a perspective based on the idea that mineralogy targets individual mineral grains, while chemistry reflects variable mixing of ingredients, as well as the issues of use and diagenesis mentioned above. He called for a complementary view of the two technical strategies, a view that is similar to the Nukuleka scenario described above (this has been advanced previously, e.g., Stoltman et al. 1992):

More often, I suspect, the most secure and geographically specific source assignments will come from studies that incorporate both mineralogy and chemistry, with the mineralogical observations clarifying ambiguities in the chemical data and vice versa (Neff 2012:245).

This thesis is concerned specifically with a geochemical approach to ceramic analysis, particularly using handheld instruments similar to the one employed by Burley and Dickinson (2010). The broader research goal, however, is to contribute to archaeologists’ ability to pursue complementary analyses such as the one described above. The detailed research problems of this thesis are outlined, following a more in-depth discussion of ceramic geochemistry as research strategy.
Ceramic geochemistry: goals and approaches

In most parts of the world, pottery dominates archaeological assemblages post-dating the societal changes associated with the Neolithic (or regional equivalents) (Pollard and Heron 2008:99) and has been used everywhere to construct chronologies. Ceramic geochemistry, however, has made major inroads in only a handful of regions. An informal survey of literature on ceramic geochemistry reveals a predominance of studies utilizing materials from the American Southwest (e.g., Abbott et al. 2012; Duwe and Neff 2007), the Mediterranean (e.g., Neyt et al. 2012; Schwedt et al. 2004, 2006), the Middle East (e.g., Attelmanan and Yousif 2012), Western Europe (e.g., Finlay et al. 2012; Kahl and Ramminger 2012), East Asia (e.g., Ma et al. 2012), and an emerging geochemical focus in Oceania (e.g., Burley and Dickinson 2010; Golitko and Terrell 2012). This pattern is likely explained in part by the relative importance of ceramic research to investigations of trade and migrations in these culture areas.

Ceramic geochemistry is performed using a variety of analytical techniques, most of them requiring the aid of technologists with substantial expertise in the appropriate physical and chemical fields. One commonly-used technique is neutron activation analysis (NAA), which rose to prominence in archaeology in the 1970s and 1980s, and is still preferred by some for its precision and bulk analysis capability (Neff 1992). X-ray fluorescence (XRF) is another technique, prized for its speed, cost-efficiency, minimal sample preparation, and non-destructive capability (Shackley 2011).

In the early years of ceramic geochemistry, archaeologists required access to nuclear reactors that existed in a limited number of laboratories (Neff 1992), and in addition to the expertise required to operate this equipment, their work also necessitated the use of state-of-the-art computing facilities to process the multivariate data. While
updated versions of these large laboratory-based techniques are still in use, several developments have made geochemistry more widespread and easily accessible. Innovations such as tabletop and handheld analyzers allow for rapid, cost-efficient analysis, with real-time data acquisition and rapid statistical treatment. This has changed the face of archaeometry (Shackley 2010), drawing criticism of an emerging “point and shoot” mentality, and prompting such appraisals as the “pXRF Shootout” at the 2012 Society for American Archaeology meeting in Memphis, Tennessee, in which participants congregated to compare and contrast the results achievable using their preferred instrumentation and calibration protocols.

Ceramic provenance studies rely on a body of theory that combines principles of geology and anthropology, discussed in detail in Chapter 2. Any type of geochemical sourcing relies on the concept that all geological materials originate from a theoretical parent rock body, or outcrop, and that they retain a distinct chemical signature that, under ideal circumstances, may be used to trace samples to their ultimate geological origins. In practice, this simple, one-to-one scenario rarely applies. The primary distinction, however, between geochemical characterization of lithic objects and ceramics, is that ceramics are a synthetic, thermally altered product, in essence, anthropogenic “rocks”. Technological choices made by potters result in irreversible physical changes, making the easy assignment of product to source difficult. Instead, archaeologists interested in pottery production generally target communities of production, specific workshops, or even individual kilns, by amassing profile data from within and between assemblages. technique must be informed from both angles.
Thesis objective and structure

This thesis reviews theoretical and technical concepts relevant to pXRF, and contributes to this body of knowledge through the presentation and discussion of experimental data. The experiments are designed to gauge analytical variability in pXRF assays of low-fired, earthenware ceramics. They build on recent findings in the archaeometry concerning temper dilution, surface morphology, and diagenesis, with a view to understanding these issues as they interact with the unique parameters of pXRF. It is argued that the ability of pXRF to “average” the geochemistry of the sample is, for the sake of ceramic analysis, advantageous.

Beginning in Chapter 2, background regarding provenance research is outlined. This is followed by a discussion of ceramic technology, and the role of ethnoarchaeological studies informing ceramic compositional research. Here I outline a theory of ceramic composition that acknowledges the environmental and technical factors that contribute to the geochemical signature of an artifact.

Chapter 3 gives an overview of technical issues around X-ray fluorescence and its use in archaeometry. The chapter concludes with a look at recent applications of pXRF in archaeology.

Chapter 4 presents the rationale, methodology, and results of the primary experimental component of the thesis: a systematic program of repeat pXRF on ceramics aimed at exploring compositional variability. This is followed by a discussion of the results as they relate to the theoretical issues considered earlier. Chapter 5 presents the results of a case study, using an expanded sample of ceramic artifacts from the Sigatoka Sand Dunes in Fiji.
Chapter 2: A theory of ceramic composition

In *Pottery Analysis: A Sourcebook*, Prudence Rice (1987) gives precedence to technical aspects of pottery manufacture before describing techniques for archaeological analysis – a structure that acknowledges the importance of understanding what pottery is made of, and why, before attempting to measure, characterize, or quantify pottery from archaeological sites. In this thesis, I follow this example. I outline some of the many factors that contribute to the geochemical makeup of a ceramic artifact, as elucidated through experimental and ethnoarchaeological research. In doing so, I provide a broader context for discussing the use of pXRF to address questions of ceramic provenance.

Because I make a clear distinction between obsidian-style sourcing and ceramic compositional studies later in this thesis, it is important to first explore the full extent and origin of ceramic composition. I begin, however, by discussing the key concepts related to provenance and sourcing that have become common in the archaeological literature.

Misconceptions abound in the realm of archaeological “sourcing studies”, even amongst active archaeologists, particularly in the conflation of the separate but related processes of characterization and source identification. Although straightforward, one-to-one “matching” of samples to sources does indeed occur, archaeologists specializing in materials analysis are concerned with the full spectrum of production: “… [artifact] technology as extraction, manipulation, transformation, and exchange of matter” (Butzer 1982:162). This view is particularly appropriate in the case of ceramic compositional studies. The composition of archaeological ceramics reflects numerous sources of variability, including environmental potentialities as well as several levels of decision-
making. Characterization of ceramics through geochemistry, therefore, generates data concerning both behavioural and environmental variability. Encoded in a compositional fingerprint are data relevant to the environmental availability and suitability of raw materials, vessel function, cultural protocols, individual preference, construction processes, and deposition of ceramic products, as well as post-depositional processes (taphonomy) and archaeological sampling protocols (Rice 1987). How to make sense of these variables in combination? Viewed skeptically, this tangled web could seem hopelessly impenetrable. On the contrary, one could view this as an information-rich “decision tree”. In this chapter I illustrate how interpretation in compositional analysis is aided through ethnographic analogy and experimental research.

While ceramic geochemistry has enjoyed over half a century of methodological development and fine-tuning, theoretical considerations only began in earnest during the 1970s and 1980s, at the height of debates on Middle Range theory, evolutionary theory, and cognitive anthropology (Rice 1996). This chapter considers the theoretical context for contemporary ceramic geochemistry, which I argue is necessarily rooted in ceramic ethnoarchaeology and experimental archaeology. Researchers in both of these diverse fields have contributed to an understanding of variability in ceramic technology. This chapter begins with a review of characterization, provenance, and source, and how these concepts apply to archaeological ceramics.

Ceramic provenance and sourcing in archaeological context

Research into the physical and chemical attributes of pottery dates back to the late 19th century, with mainstream interest, particularly in mineralogy, beginning in the 1950s (Neff 1992). Pioneering geochemical studies using nuclear techniques were largely
concerned with developing effective methodologies for demonstrating trade and commerce (e.g., Sayre and Dodson 1957), an interest that has not waned after decades of development. This period was characterized by a renewed and intensified interest in ceramics, culminating in the late 1950s “ceramic sociology”, in which archaeologists such as Longacre, Spaulding, and Deetz placed emphasis on patterning in ceramic stylistic attributes in an attempt to identify types and reconstruct social systems (O’Brien et al. 2005:68). A precursor to the work of Binford and the New Archaeology, this school of thought integrated stylistic, physico-chemical, and ethnoarchaeological data explicitly for the first time in order to address questions about social structure, materials production, human-environment interaction, and trade and exchange.

In reviewing contemporary archaeometry literature, it becomes apparent that these research goals remain fundamentally intact. Beyond low-level observations based on matching artifacts to geological sources, chemical approaches to ceramic research aim to “draw greater anthropological meaning from compositional differences” (Alex et al. 2012:821).

According to Butzer (1982:161), the significance of raw material characterization is twofold: an understanding of technological aspects of artifacts, and the identification or estimation of source areas involved in exchange networks. Orton et al. (1993:145) make a further differentiation between the compositional comparison of artifacts in which the origins of some are known, referred to as workshop sourcing; while other studies may try to compare the paste composition of sherds with no known origins in order to develop useful groups that may or may not reflect culture- or source-areas.
Source

The definition of source may differ, depending on the opinions or experience of the investigator, the aims and goals of the research, and the material used for analysis. It is important to note that source can almost always be viewed as a heuristic, theoretical construct, based on probabilities; it is also scalar, depending on the research question. Source may refer to an individual, geographically restricted area, which is sometimes appropriate in the case of volcanic rocks that can be associated with specific flows (Binder 2011; Tykot 1998). More often, however, source is used to refer to larger areas where geologically related raw materials can be accessed. In the case of obsidian, this could mean an entire volcano, which can encompass several chemically unique volcanic glasses. While the latter view is certainly more appropriate for understanding ceramic sources, it is not fully adequate.

As discussed in further detail below, ceramics generally comprise two primary sets of materials: raw clay, and tempering agents, most commonly made up of mineral or calcareous sands. These two sets of materials both make a contribution to the chemistry of the artifact, and need not overlap geographically in their natural distribution. For this reason, among others, Bishop et al. (1982:276) recommend the use of a zonal approach for ceramic sources, a concept related to the resource procurement and “catchment area” models most fashionable in the 1970s and 1980s but still largely relevant today. The ideal scenario involves the creation of geographic “microzones”, in which certain specific raw materials can be found, and which shrink in size as analytical techniques become more sophisticated and more studies of an area are completed (Bishop et al. 1982:276). This strategy is mirrored by Rice (1996:172): “…varying levels of increasing inclusiveness of compositional data are interpreted as paralleling various
levels of geographical inclusiveness, conceptualized from the individual clay mine to the cultural region”.

This perspective has its origins in earlier work. Dean Arnold (1971; Arnold et al. 1991), an ethnoarchaeologist working among contemporary Maya potters, constructed experimental ceramic “source” groups, which he referred to as a “general ethnographic groups”. This was accomplished by sampling all known clays and tempers in the study region, mixing them in every possible combination, and plotting the chemical fingerprint of each combination to form a large, hypothetical compositional group. Interestingly, ethnographic pottery samples from the region, constructed using various combinations of these raw materials, all produced chemical data that fell within the expectations of this hypothetical group (cf. Arnold et al. 1991:Figure 9).

Source is consistently problematic in ceramic sourcing studies. As discussed in further detail below, the chemistry of a raw clay source rarely matches easily with the chemistry of a finished ceramic artifact. Source, then, must be a flexible term, flexible to change as the individual circumstances of ceramic production come to light. It may, in the end, be used to refer to a specific clay “mine”, but more frequently source is used to refer to larger geographical areas, watersheds, or individual river systems. When sampling of raw clay is problematic, ceramic sources are sometimes defined by the production centers from which they originated. Compositional group, in these cases, becomes the more relevant term, and is defined below. While finished artifacts may not chemically “match” the raw clays used in their manufacture, sampling on a large scale has the potential to identify generalized regional profiles under which individual samples could be subsumed (Arnold et al. 1991).
Characterization versus sourcing

The distinction between characterization and sourcing is essentially one of logical steps in open-ended process. Characterization refers to a suite of techniques and methodologies for qualifying or quantifying the compositional attributes of materials. These methods begin at basic visual characterization (sorting materials based on colour or texture), and include all mineralogical (petrographic) and chemical techniques. Characterization is an essential step in identifying relationships between artifacts and sources.

Geochemical characterization can be qualitative (establishing the relative concentration of elements) or quantitative (establishing absolute amounts of specific elements, usually given in parts per million). Sourcing occurs when the composition of an artifact is shown to fall within the expected range of physico-chemical variation of a source material. This criterion alone does not generally satisfy the burden of proof for confident sourcing, as the relationship between artifact and source must also meet expectations based on probabilities and past experience. Sourcing is best framed as a testable hypothesis.

Chemical fingerprint

Generally interchangeable with “profile” or “signature”, chemical fingerprint is defined by Bishop et al. (1982:294) as “… a weighted average of all the mineralogical components of a ceramic specimen”. Because certain elements occur commonly in nature (e.g., Fe, Si, Al, Ca, Na), geochemists generally rely on the relative abundance of trace elements (less than 1000 ppm or 0.1% of composition) to discriminate between chemically distinct
objects. Most chemical fingerprints of archaeological materials are based on configurations of trace elements.

An important and related concept for definition is the *compositional group*, used throughout the sourcing and provenance literature and in this thesis. A compositional group is a statistically determined cluster of data points (in many cases, representing individual artifacts), which occur at variable distances from a group centroid. In multivariate statistical treatments of chemical data, variation in elemental composition is synthesized and combined to form variables such as components, or factors, depending on the treatment applied. These reduced variables can be graphed to display clustering in variation (Figure 1). Statistical concepts relevant for this thesis are discussed in a later chapter. Sourcing is accomplished when the chemical fingerprint of an object falls within the expectations of a compositional group, defined either by direct sampling of raw materials or through analysis of other artifacts.

**Provenance and abundance**

There is debate over the appropriate use of provenance versus provenience. Provenance is used throughout this thesis, and in the most general sense refers to the origin of an object, either geographically or culturally as the circumstances dictate. The archaeological “provenience postulate” is a generalized set of assumptions, best styled as a hypothesis: geochemical differences exist between raw material sources (lithic, clay, or otherwise), which can be identified using the appropriate analytical technique; further, compositional variation within a source should be less than the variation between sources (Bishop et al. 1982:301). The latter half is particularly important, and not only for ceramics. Significant intra-source compositional variation is noted for obsidians, which
are commonly thought to occur in relatively homogeneous outcrops (Shackley 1998b). Intra-source variation can lead to the erroneous definition of compositional groups.

Another important heuristic assumption is the “criterion of abundance”, which holds that the most abundant category, or unit, evident at a site is the most likely to be of local manufacture, while categories that are less represented tend to reflect importation of non-local items (Bishop et al. 1982:301). Applied to compositional analysis, artifacts falling within the most abundant compositional group are more likely to be of local manufacture than those belonging to less abundant compositional groups. Important exceptions will, of course, arise; one need only imagine a scenario in which groups or individuals produce little or no ceramic material culture, preferring to exchange their own
specialized goods for ceramic products made elsewhere by other people. In pottery-
producing societies, however, ethnographic generalizations indicate that the majority of
pottery used in ordinary aspects of life is produced using materials within a several-
kilometer radius of the residential area (Arnold 1971, 1985).

A critical addition to these concepts, in the case of ceramic compositional
analysis, is the alteration to raw clay that occurs during the procurement and processing
of raw materials, the use of the artifacts, and their post-depositional context and history.
The problem is summarized well by Rice (1978:514):

The basic ‘assumption’ of pottery provenience studies may be stated as a
null hypothesis: that at no time during pottery manufacture or use
(including all steps of clay selection, paste preparation, forming and
decorating, drying, firing, use, and discard) is the trace element
configuration characteristic of a raw clay deposit significantly altered. This
‘assumption’ is a tenuous one, for it covers a wide range of circumstances
of conscious and unconscious choice, values, and motivations on the part
of potters and random and non-random factors of geochemical
composition and behavior of clays. In other words, it implies that none of
the additions or extractions of substances to or from a raw clay, or
thermal changes in the firing of a clay, or leaching or alteration after
discard of the fired object, affect its trace element pattern.

It is abundantly clear that the idealized expectations of archaeological sourcing
studies, as discussed in the above definitions, come into conflict with what
archaeologists know about ceramic technology. Various interrelated factors, both cultural
and non-cultural, contribute to variability in ceramic paste composition, and must be
controlled for in materials characterization research. The following sections discuss the
ways in which the more salient of these issues have been explored through
ethnoarchaeological research and experimental archaeology.
Variability in ceramic composition: ethnoarchaeological investigations of ceramic technology

Ceramic ethnoarchaeologists have studied contemporary potters and pottery to help solve a range of archaeologically relevant problems, by providing data upon which to base inferential interpretations of ceramic material culture (Stark 2005). For example, Krause’s (1985) account of African pottery production, which encompassed material selection and procurement, production, decoration, firing, and other aspects, resulted in a “grammar” of pottery production which could be considered in archaeological contexts. Such studies have also told us what we know about use, transport, and exchange of pots in traditional economies. Importantly, each of these areas of study is relevant for making interpretations based on geochemical or mineralogical data, as they all provide behavioural correlates for compositional signatures. This section reviews ethnoarchaeological contributions relevant for ceramic geochemistry.

Raw material selection and procurement

While ceramic production is only one traditional arm of ceramic ethnoarchaeology, several scholars have made the technical factors of ceramic production a particular focus, Dean Arnold being one of the more prominent of these researchers (Arnold 1971, 2000, 2008; Arnold et al. 1991). Mirroring an archaeological interest in geochemistry and ceramic provenance, Arnold (1971) conducted ethnoarchaeological research with Yucatan Ticul Maya potters for decades that focused on raw material selection and production techniques, an approach he dubbed “ethnomineralogy”. His interest through these studies was how raw material procurement in contemporary societies can strengthen archaeological inference based on ceramic composition (Stark 2005:203).
Arnold (1971) initially approached the problem from the perspective of cognitive anthropology, which, broadly conceived, investigates the way people of different backgrounds perceive the world. Arnold and other anthropologists of this school were particularly interested in applying this body of theory to material culture, identifying the material outcomes of cultural systems. Arnold (1971) framed the problem of ceramic paste composition as a matter of matching “emic” decision-making about raw material selection with “etic”, external observations, adapting these terms as developed by Kenneth Pike (1954). Arnold was interested in “cognitive maps”, or, the sets of knowledge and concepts shared by members of groups at various levels. Of particular interest here are Arnold’s attempts to define group parameters based on shared cognitive concepts – in this case, the knowledge of which clays and tempers are appropriate for different vessel types, and where to find them. This drives right to the heart of how compositional analyses are understood archaeologically and anthropologically: to what extent do chemical compositional groups reflect culturally- or behaviourally-relevant categories?

Arnold (1971) followed the work of several Yucatan potters as they sourced the raw clays and tempers used in their craft, collecting his own samples for later analysis using X-ray diffraction, a technique that identifies specific compounds present in the sample. Worldwide ethnographic data suggest that most traditional potters acquire their raw materials from no more than 7 kilometers away from the production center, and in most cases under 3 or 4 kilometers (Arnold 1985:38; Arnold 2000). Arnold conducted work in an area where both clays and tempers are “mined” from specific locales, and subject to social and political boundaries. While Arnold favoured traditional explanations of resource procurement based distance and energy expenditure, he was able to demonstrate conclusively that raw material sources had specific meaning and were
sought out for specific reasons; Ticul Maya potters do not simply use whatever sand is closest at hand. Potters were even observed purchasing quantities of specific tempering agents, prized for specific qualities, with cash (Arnold 2008:214).

Arnold demonstrated that composition, as viewed archaeologically, can be affected by sociopolitical boundaries and other factors that leave only scant traces in the material record. Patterns in composition are more easily detectable. Arnold argued that the only way to bridge the “divide” between ethnographic or “emic” knowledge and external, “etic” observations, was through analogical inference, employing social theory. His work has contributed to a general body of theory that relates ceramic paste composition to social patterns of raw material preparation and procurement (Arnold 2008). Indeed, as Rice (1996:190) argues, the technical aspects of pottery are where analogical inference are the strongest and most appropriate.

A similar strategy has been usefully employed more recently by Stark et al. (2000) among traditional Kalinga potters in the Philippines. Clay and pottery samples collected in several communities in the late 1970s and 1980s, during a long-term study by Longacre and colleagues (Longacre 1981, 1991; Graves 1991), revealed important compositional differences using NAA that related to their technological and behavioural contexts. While function was one factor, it was clear in the Kalinga case that social relations were equally important in material selection. Studies such as these reveal several layers of nuance and contingency to more simplistic models of resource procurement based on distance (Costin 2000:380). Connell (2002) has applied ethnoarchaeological observation to questions about the physical extraction of clay and its relation to areas of production in Mesoamerican contexts. Other scholars have opted to follow Arnold’s (1971) approach to ethnomineralogy. Munita et al. (2005) employed
chemical and mineralogical techniques to raw clay and finished ceramic samples, in order to study raw material choices made by Asurini potters in Pará, Brazil.

Why do potters choose to use specific materials, even when others are available? Rye (1976:108) provided one answer:

These reasons are not recoverable archaeologically. What are recoverable are patterns of material use at the etic level. If similar specific materials are used by potters widely separated in time and space we can ask: ‘what technological advantages do these materials offer when used to make vessels of x function or y technique?’ If answers to this question can be found then we are beginning to understand strategies adopted by the potter in using his material environment.

Rye emphasized environmental availability and material workability in raw material selection, stemming from his fieldwork in Papua New Guinea. In particular, he observed potters making decisions based on functional considerations such as thermal shock resistance (Rye 1976:113), which confers the ability to withstand repeated heating and cooling associated with cooking. Thermal expansion during firing can also play a role, as some clay minerals expand more than other during firing. Clays that have low expansion during firing may therefore be preferable.

Other work emphasizes material selection based on less tangible or less immediately discernible criteria. Leblanc (2011, 2012) documented a unique tradition of traditional pottery production on the island of Kadavu, Fiji. The potters of Nalotu Village revealed an oral tradition governing the selection of raw clay and temper sands, based on the story of the arrival of the first woman potter to the island. In a beachfront environment, with plentiful sand at hand, the potters of Nalotu continue to travel to a single location to retrieve temper sands, a pond that the first potter is said to have bathed in upon arrival on Kadavu.
Clay processing and preparation

It is well-documented ethnographically that traditional pottery-making often involves a process by which raw clays are processed and altered to achieve maximum workability and strength when fired. The most common processes are clay “washing” and levigation, during which clays are dried, pounded, and suspended in water. In most cases these processes are designed to remove coarse or foreign materials from the clay, before the potter introduces their own preferred tempering agents into the mixture. Clays are often kneaded heavily, and some are stored for long periods of time to “age”, which is said to give the clay greater workability (Hamer and Hamer 2004:345; LeBlanc 2011:56).

Washing and levigation can add or remove material from a raw clay, and it has been demonstrated that the water used in these processes can introduce contaminants (Arnold et al. 1991; Orton et al. 1993:146). Bishop et al. (1982:294) and Rice (1978:549) pointed out that soluble compounds containing Na, K, Mg, and Ca are particularly susceptible to differential removal when clay is washed. Rye (1976:120) noted that the use of saltwater in clay processing will naturally introduce greater levels of Na into the paste mixture, and could impact the function of the vessel during use. Blackman (1992) demonstrated that “size sorting” of sediments (removal of coarse fraction from finer clay particles) can have an impact on elemental concentrations, as coarser particles will act as natural “diluents”. Clay particles, as defined in the Wentworth scale of grain sizes, are generally below 4 μm.

While much of this behaviour can be interpreted through a functional lens, Smith (2000) argues that clay processing behaviours observed in Cameroon are not readily explicable through a techno-functionalist framework:

… none of the parameters theoretically considered to influence technical behaviours – techno-functional or environmental requirements, identity,
economic status of the craft, learning networks, distribution networks and settlement pattern – taken alone are sufficient to explain technical variations in the Faro area (Smith 2000:36).

The distinction drawn by Smith between ‘cultural’ (by which he means “social/symbolic”) and ‘technical’ interpretations is perhaps not as wide in the contemporary literature as it was then, but it provides a useful framework to view the related and unrelated factors influence variability in ceramic paste composition. This divide is further reflected in Figure 2 in the concluding section of this chapter.

**Tempering**

Temper refers to any non-plastic additives mixed into raw clay to produce a paste that meets the specific needs of a potter. While the most common categories of temper are mineral and calcareous sands, other additives include grasses (chaff) or other vegetal matter, animal dung, crushed shell or bone, volcanic ash, and crushed pottery (‘grog’ temper). Rye (1976:109) discusses four primary reasons why tempers are added to ceramic pastes: workability, to prevent the clay from being too sticky or cracking when forming the vessel; shrinkage, as temper will help a vessel to dry evenly without cracking in the process; firing behaviour, as temper will evenly distribute heat and prevent breakage; and fired properties. Depending on the tradition of manufacture, some potters may prefer certain types of temper for vessels intended to hold water, cook or store food, or any other intended function.

It is well-documented that choices made by potters concerning the type and amount of temper to use in their paste ‘recipes’ is, in most cases, not random and not based on immediate availability. Many of the reasons for choosing tempers may be regarded as “functional”, in the sense that they confer desirable qualities on the function
or appearance of a ceramic vessel. An example is the distinction between ideal cooking vessels and vessels intended for water storage, as noted by Rye (1976:113): In making a cooking vessel, a potter may choose to produce a more porous clay fabric that easily withstands thermal shock, and so may choose a coarse-grained sand temper, or else an organic temper that burns off during the firing process. A pot that is being heated repeatedly over fire must contain minerals that expand at a similar rate as the fired clay itself to avoid fracture (Rye 1976:114). The ideal water vessel, however, requires finer pores and perhaps a lighter colour to reflect heat. A fine calcareous sand would be one possible choice. Rye (1976:119) reports that the majority of ethnographically documented Melanesian wares contain minerals with relatively low rates of expansion: calcite from calcareous beach sand, plagioclase, hornblende, rutile, and zircon. Quartz is encountered much less frequently, possibly owing to its high thermal expansion. In many culture areas, these minerals are found in various combinations.

Several authors have drawn attention to cases of “non-functional” temper selection, as some of the cases described earlier suggest. Social and political concerns may play an equal part in the availability and desirability of specific materials (Costin 2000:380). In the Fijian example described above, raw material acquisition followed a tradition explained through the story of “culture hero”: the first woman potter to arrive on the island. Nalotu potters consistently acquire temper sands from a single pond, using the story as memory device that anchors pottery-making to place (LeBlanc 2011, 2012). Some archaeologists, eager to demonstrate this important caveat, have become rather speculative in their interpretations of temper choice. Stilborg (2001), for example, has suggested that bone and chaff tempers used in European Iron Age ceramics may have served a purpose more metaphorical than functional, in their allusion to “other objects or situations”.
Whatever the individual case may be, ethnographic inquiry has demonstrated that material selection is rarely a simple and purely functional consideration. This is an important reminder of the complexity of factors impacting ceramic paste variability. The impacts these choices have on the archaeologist, in trying to characterize this variability, have been explored experimentally for decades.

**Variability in ceramic composition: experimental research on paste variability**

In the ethnoarchaeological literature reviewed above, researchers aimed to understand ceramic technology and sources of compositional variability in ceramics through ethnographic observation of raw material procurement, clay processing, and ceramic production. Archaeometry has long been interested in the measurable outcomes of potters’ technical choices. Other sources of variability are not observable in the field, and require scrutiny in laboratory settings. Specialists in technical aspects of ceramic geochemistry have conducted experiments aimed at demonstrating the effects of different variables on ceramic composition. Many of these studies use experimental or archaeological specimens to understand the specific impacts of factors affecting instrumental precision and replicability. The review below is organized into major categories of technical importance: the effects of temper types and temper dilution, the impacts of varying drying and firing strategies, and the results of post-depositional alterations on paste composition. These factors relate to the proportional dilution or enhancement of trace element signatures in raw clay. Many of the studies reported here are concerned with removing or controlling for the contaminating effects of tempers, either through physical, chemical, or mathematical means.
Temper type and the problem of “dilution”

Geochemical “fingerprints” are often based on unique configurations of major, minor, and trace elements. Because clays represent the “end point” or product of geological processes, trace elements are generally more concentrated than in other types of deposits (Bishop et al. 1982:294). Clay itself refers to a particle size, (4 μm and under, according the Wentworth scale). Many minerals, therefore, can become clay-sized particles after weathering. Clay mineral is a separate term, referring to a group of sheet-like minerals related to mica (phylllosilicates) that tend to occur and dominate in clays.

The addition of tempers, which are generally coarser-grained than the fine particles which make up clay, can either dilute or enhance the signature of specific trace elements as the homogeneity of the pure clay is disrupted. It is a matter of proportion. Addition of relatively pure quartz sand will tend to dilute trace elements in the clay paste, unless significant amounts of zircon are present, as it contains high concentrations of rare earth elements (Bishop et al. 1982:295). Shell temper has been shown to affect paste chemistry in various and unpredictable ways (e.g., Cogswell et al. 1988). Volcanic sand and grog temper tend to affect trace element concentration the most.

This “problem” of temper dilution has been an object of considerable research, with the ultimate goal of understanding the qualitative and quantitative chemical impact of temper additives to raw clays. This stems from an interest in sourcing ceramic artifacts to the source of their raw clays, a theoretically interesting but methodologically problematic pursuit. As the above sections begin to detail, the modifications to raw clays, regardless of their mixture with tempers, have the potential to render them chemically distinct from their parent clay beds. Nonetheless, various techniques for investigating the impact of temper have been attempted.
“Dilution” refers to the proportional change in elemental concentration when tempering agents are added to a raw clay. A calcareous temper, for example, when added to an iron-rich clay, will cause the overall composition of the ceramic to be lower in iron than the clay itself. Neff et al. (1988, 1989) conducted a series of simulation analyses to estimate the degree to which two distinct clays could be made to “overlap” chemically by the addition of a single type of temper. In an archaeological scenario, this would impact the ability of the analyst to distinguish between the two clay types, and could result in erroneous interpretations. They conclude that highly heterogeneous tempers are more likely to cause this obfuscation, while homogeneous tempers are unlikely to cause distinct clays to overlap. The “upshot” is that clays and tempers react in various ways, and can have unpredictable effects on the mathematical treatments applied to the raw data; as Rice (1996:170) rightly points out, however, the use of simulations on “theoretical” clays only partly reveals the true nature of real clays and their variability in real-world settings.

Of particular interest in this branch of archaeometry has been the impact of calcareous sands and crushed shell. Cogswell et al. (1998) wanted to understand the elemental dilution and enhancement effects of tempering ceramics with crushed shell, which is known to contain numerous contaminants and high concentrations of several trace elements. The researchers manufactured experimental briquettes with natural clays, tempering some with burned and crushed shell, as is common in Mississippian ceramics. Chemical assays of the briquettes found that the shell-tempered briquettes were chemically distinct from the untempered briquettes, containing significantly higher amounts of Ca, Sr, Na, and Mn. They proceeded to evaluate a chemical method for removing the effects of shell, which has been used at times in the past. Shell-tempered briquettes were leached using HCl, which was successful at diminishing the impact of
Ca and Sr, but also unintentionally lowered the concentration of 22 other elements. Cogswell et al. (1988) argued that mathematical correction procedures were more effective, and were successful at returning the values of the tempered briquettes to "normal" mathematically.

Steponaitis et al. (1996) similarly factored out the effects of shell temper from their sample of Mississippian ceramics using mathematical corrections. Broadly, these procedures involve the removal of Ca and Sr (Sr occurs in high concentrations in shell), and recalculating the other elements to correct for the diluent effects. This approach may be problematic in its assumption that shell is the only source of Ca in ceramics; Ca is often present in varying amounts in ceramics tempered with non-calcareous additives, such as when organic content is present on the surface or within the matrix of the ceramics, or when tempers contain Ca-rich feldspar sands.

Some researchers have attempted to physically remove mineral inclusions from fired clay pastes, notably through the use of ultrasonic disaggregation. This destructive, labour-intensive strategy has been attempted on several occasions, with moderate success (Cogswell 1998; Elam et al. 1992; Gaines and Handy 1977). The process involves manually crushing ceramic sherds and immersing them in an ultrasonic waterbath, a commercially available appliance used to clean delicate or intricate items such as jewelry or industrial parts. High frequency sound waves cause microscopic air bubbles to form rapidly and implode (cavitation), an action that penetrates cracks and pores and loosens adhering materials. The resulting "slurry" is centrifuged to separate the coarse fraction (natural or added aplastic tempering agents) clay mineral fraction from the water. The fractions may then be analyzed separately.

Summerhayes (1997) used microprobe and PIXE-PIGME (proton induced X-ray/gamma-ray emission) analyses to overcome the "chemical noise" of natural and
added mineral inclusions in ceramics from Buka Island, New Guinea. An electron microprobe instrument is capable of analyzing the composition of very small objects, in this case, individual temper grains.

Sterba et al. (2009) conducted tests similar to the simulations done by Neff et al. (1988, 1989), but using real clays and tempers in various combinations to determine the statistical effect of each. The researchers used neutron activation (NAA) on their experimental tiles. They once again demonstrated the possibility of mathematical correction for removing the diluting effects of tempers. In another study, Sterba et al. (2012) used μ-spot (microbeam) analysis to characterize individual temper grains, strengthening the calculations that factor out dilution.

Many of the studies described above are interested in estimating the chemistry of the original clay, which we know to be altered through firing and initial processing. Of critical importance in any physical, chemical, or mathematical removal of the contribution of temper to paste chemistry, is the understanding that processed, fired ceramics are already irrevocably altered, and will never again fully reflect the natural chemistry of a raw clay source. Alterations to the clay do not, however, end with the production and use of a ceramic artifact; indeed, physico-chemical changes continue in the post-depositional environment of the artifact, and its subsequent recovery and curation by archaeologists.

**Drying and firing**

Certain elements are known to undergo changes at pottery firing temperatures. The impacts of drying and firing on the composition of clays have been explored by archaeologists for several decades. While this type of research is sometimes conducted in ethnoarchaeological field settings (e.g. Rye 1976), the majority of work on this
problem has occurred in the laboratory using experimental ceramics. A few key studies are summarized here.

Kilikoglou et al. (1988) collected raw and processed clays from different locations on the island of Crete. The clays were purified, characterized using neutron activation analysis, then fired at different temperatures. The fired tiles were analyzed for evidence of compositional change due to firing. The authors found no evidence of volatilization in 20 minor and trace elements. Finer purified clays were found to have higher concentrations of trace elements, which was expected, given that soluble elements were removed during the purification (cleaning) process. Firing did appear to increase some elemental concentrations, which the authors attribute to the final traces of water being evaporated and organic substances being combusted.

Cogswell et al. (1996) produced a series of experimental ceramic tiles and fired them at temperatures ranging from 100°C to 1100°C. The tiles were analyzed using neutron activation before and after firing. The authors found no volatilization in 34 elements. The one possible exception was Br, which mirrored findings in earlier studies.

Schwedt and Mommsen (2007) demonstrated the influence of drying and firing on the formation of trace element “profiles”, that is, differences in the concentration of certain trace elements at the surface and the center of a ceramic object, before and after the drying and firing process. Using experimental fired clay briquettes, they found that As was lost during the firing of some clays. In addition, in clays containing NaCl, sodium migrated to the surface during firing. In clays containing both NaCl and calcite, the heavy alkali elements Rb and Cs evaporated from the surface, leaving distinct trace element profiles in the experimental ceramics.
Firing does not appear to be a major source of compositional variability, particularly in low-fired earthenwares. Nevertheless, fluctuations in scarce elements still have potential implications for multivariate statistical techniques, as discussed below.

**Post-depositional alteration**

Ceramic fabrics are not physically or chemically inert after use and deposition, as a number of archaeological and simulated examples have demonstrated. Reactions include a range of leaching and absorption processes that vary with the post-depositional environment. Some reactions are general and predictable, while others are case-specific; for example, ceramic vessels recovered from seawater can absorb large quantities of Mn, while absorption of phosphorus is reported in areas where modern chemical fertilizers are used (Orton et al. 1993:147). This section reviews several studies aimed at demonstrating the cumulative compositional changes that can occur in pottery after it enters the archaeological record, processes encompassed by the term, “diagenesis”.

Franklin and Vitali (1985) subjected experimental ceramics to a variety of corrosive solutions to mimic the effects of long-term deposition, in some cases as long as 16 months. In addition to monitoring chemical changes in the ceramics themselves, using X-ray fluorescence and X-ray diffraction, they also tested the liquid solutions in which the tiles were immersed for evidence of compositional change using neutron activation analysis. They noted initial chemical reactions at the surface of the ceramic tiles that stabilized after a short time. The ceramics apparently built up protective layers, or “patinas”, at the surface that prevented any major reactions in the cores of the samples. These authors noted that cracking through freezing or trampling would create new reactive surfaces, and argued that chemical alteration is tightly linked with the
physical integrity of the artifacts. This study highlighted early on the differential changes that can occur at the surface and at the core of a ceramic sample.

Schwedt et al. (2004) employed a strategy of taking surface and core measurements to demonstrate this differential change in archaeological samples. They sampled 38 Mycenean sherds with “corroded surfaces” (soft or brittle, likely from sun or water exposure) and tested surface and core samples using neutron activation analysis. They found significant changes in Ca and the alkali metals Cs, Rb, K, and Na, as well as rare earth elements Sm, Eu, and La. While elements in the latter category would normally be excluded from compositional analyses, due to their low occurrence, the authors suggest that changes in these and other rare elements may explain why around 10% of “singles” occur in statistical groupings (i.e., changes the ratios of these elements result in erroneous compositional groupings) (Schwedt et al. 2004:96). The authors’ demonstration of Ca leaching mirrors simulated findings by Cogswell et al. (1998), described above.

Schwedt et al. (2006) make similar surface-core comparisons using both neutron activation and X-ray fluorescence analysis, finding that each technique is more sensitive to different types of alteration. They argue that both should be used in a complementary fashion.

Recently, Golitko et al. (2012) convincingly demonstrated uptake of barium by New Guinea ceramics. Using laser ablation-inductively coupled plasma-mass spectrometry (ICP-MS), the authors mapped compositional profiles on fresh-cut samples of pottery, indicating concentration gradients in Ba from the core to surface.

In addition to adding another potential source of compositional variability in ceramics, diagenesis has also been shown to impact the results of other archaeometric techniques. Zacharias et al. (2007) demonstrate the impact of K leaching in calcareous
Roman ceramics on thermoluminescence (TL) dating. They use the overestimated TL dates to model and date the timing of the alteration, suggesting the majority of K leaching occurred shortly after deposition. Surficial diagenesis can also lead to significant visual differences, as argued by Tschegg (2009). Tschegg shows how a natural corrosive process can result in a whitening of the surface of a sherd, leading to the erroneous interpretation of an intentionally-applied white slip.

**Summary: sourcing anthropogenic rocks**

This chapter has reviewed key concepts that are central to research employing techniques borrowed from the physical sciences to study production and exchange in past societies. In a sub-discipline that has devoted considerable effort to methodological development and fine-tuning, it is prudent to view materials analysis in broader theoretical context. Of particular significance to this thesis project are the many sources of compositional variability in ceramic artifacts; globally, ceramics encompass an extensive suite of diverse technologies, with a range of complexity that this review has only begun to explore. They are perhaps best viewed as diverse, but related, anthropogenic “rocks”.

To the outsider, unaware of such complexities, but interested or invested in the outcome of archaeological sourcing studies, the seemingly overwhelming potentialities and contingencies of this process need not be cause for avoidance. Geochemical and mineralogical research in archaeology is conducted on an increasing scale and with fruitful results, on all categories of material culture. The suite of technologies available for this type of research is growing in number and in sophistication. An important development in this area is the emergence of commercially-available, “user-friendly”
technology, which puts the power of physico-chemical analysis into the hands of the field archaeologist. This class of technology, and the primary subject of this thesis project, is described in detail in the following chapter.

This chapter began with a series of definitions of terms used in compositional analysis and sourcing, with particular reference to ceramic geochemistry. Importantly, characterization and sourcing were distinguished as logical steps in a process. This distinction is mirrored in the broader archaeological aims of compositional analysis: before you can talk about trade, you need to focus on aspects of production. As Bishop et al. (1982:276) note:

[Sourcing] may be done directly, by establishing probable relationships of pottery to geographically localized raw materials, or indirectly, by demonstrating differences in ceramic pastes [to] indicate the existence of geographically isolable resources.

Source itself was discussed, giving a sense of its complexity. As an analytical concept source can refer to a physical, geographic point in the cartographic sense, a group of related technologies, a community – the meaning changes depending upon the aims of the research. As discussed throughout the remainder of the chapter, source in the context of ceramic artifacts can equally mean a clay deposit, and source of temper sand, a potter’s workshop, a village of potters, a region, or an archaeological point in time. It is apparent that the chemical signature of a ceramic sherd could contain information exceeding in importance the location of the raw clay used in its manufacture.

It was argued in this chapter that contemporary ceramic geochemistry derives much of its theory from two primary sources: ethnoarchaeological investigations of ceramic production in traditional societies, and experimental studies of paste matrices and the many factors that impact their compositional signature. Ethnoarchaeological
research has been especially informative on aspects of raw material procurement, particularly with the revelation that potters do not always use clays and tempers that are closest at hand. Observational research has revealed the many transformations and alterations a raw clay goes through in its journey to become a useful ceramic vessel, making the idea of matching the chemistry of raw clay to a fired vessel seem improbable. Importantly, these modifications are not universal, and can indeed come down to individual preference. Rather than viewing these processes as the irreversible loss of scientifically observable data, one could instead choose to focus on the idea that each them involve the transmission of knowledge and exist in a (past) cultural context.

Experimental studies have equally revealed important understandings of the technical aspects of ceramic production, use, and deposition. Of particular importance for this thesis project is the study of diagenetic effects, or post-depositional alteration. After clay is transformed into a vessel, encoding all of the cultural information described above, it still endures the destructive effects of years underfoot, underground, or underwater. Several of the studies reviewed in this chapter described how erosion, leaching, and absorption can affect elemental concentrations in ceramics, and how this may impact paste analyses that rely on the identification of unique configurations of trace elements. In addition, experimental research has investigated the impact of differing types and amounts of temper on the chemical composition of ceramics. While quantifying this effect may be useful in cases where individual raw clay resources are being distinguished, I argue that temper need not be treated as though it were a contaminant; rather, the specific combination of clay and temper may be equally, if not more, useful to ceramic analyst, for it reveals information concerning the specific paste recipe employed by a potter. In the way that ratios of trace elements allow lithic analysts to trace obsidians back to the volcanic flows of their origin, it is the ceramic paste recipes
that, I believe, have the most potential to lead archaeologists to the workshops in which the vessels were manufactured.

All of these factors combined have caused archaeologists employing geochemistry to reevaluate their approach to ceramic paste characterization. There exists an arsenal of highly sensitive, nuclear-powered techniques for quantifying the minute elemental make-up of artifacts, but without a critical understanding of paste composition from a social and technical point of view, they are theoretically and methodologically impotent. Like the “ceramic ecology” developed by Matson (1965; Rice 1996:184) and implemented in the work of Arnold (1971; Arnold et al. 1991) as described above, contemporary ceramic geochemistry must make it a goal to integrate physico-chemical characterization with environmental and social data. I argue in this thesis that ceramic compositional data are best illuminated by examining variability at two distinct levels: variability within the matrix of an individual artifact, and variability at the level of the ceramic assemblage. I propose a research strategy that does not attempt to remove or factor out the contribution of temper to overall composition, but rather estimates the total fingerprint of the artifact as a whole cultural product. I demonstrate how emergent instrumentation may be ideally suited for pursuing such a strategy.

Figure 2, adapted from Thompson (1991:238 figure 11.3), visually depicts the primary categories of factors ceramic compositional variability, and consolidates much of the information summarized above. This chapter has addressed, for the most part, the “non-cultural factors” and “cultural factors” on the top half of the chart. The factors on the bottom half of the chart, particularly in the “characterization” category, are addressed in the next chapter.
**Figure 2.** Factors affecting ceramic compositional variability. The top half, including the “non-cultural” and “cultural” factors is adapted from Thompson (1991:238 figure 11.3). The bottom half is my own.
Chapter 3: Theory and methodology of XRF and pXRF

Introduction

An increasingly wide variety of instrumental techniques are available to archaeologists interested in compositional analysis. The choice between techniques is dependent upon a range of factors, including the nature of the sample, cost and availability of the analysis, accuracy, sensitivity, and destructive/non-destructive capability (Lambert 2005). X-ray fluorescence (XRF) refers to a series of related techniques that are commonly used in archaeology, ranging from portable, handheld analyzers to large, highly-sensitive laboratory-based instruments. This chapter reviews the pertinent method and theory of XRF, its use in archaeology, and the range of instrumentation currently available.

The experimental component of this thesis employs a portable XRF analyzer. The second half of this chapter is devoted to unique capabilities, as well as disadvantages, of pXRF technology, its acceptance in mainstream archaeometry, and recent examples of its use.

X-radiation and X-ray fluorescence techniques

X-radiation is a form of electromagnetic radiation, much shorter than visible light, sitting between ultraviolet and gamma rays on the electromagnetic spectrum. X-rays can
penetrate solid objects, making them useful for diagnostic medical imaging and security screening.

X-ray fluorescence (XRF) exploits physical processes common to a number of geochemical techniques (Shackley 2011:16). XRF techniques allow researchers to determine the concentration of elements within samples, and to establish characteristic chemical profiles, or "fingerprints". During analysis, a sample is bombarded by primary X-rays (photons), causing excitation (ionization) of atoms in the sample to occur. This excitation causes electrons held in the high-energy central orbitals of the atoms to become dislodged and ejected. Electrons held in the lower-energy outer orbitals then fall in to replace the ejected electrons, emitting secondary, or fluorescent, radiation (X-ray photons) as they drop. Because the atomic orbitals of each element have known energy levels, this fluorescent radiation is element-specific. XRF instruments contain detectors sensitive enough to measure the intensity of this characteristic radiation, and with it, the concentration of specific elements present in the sample. Other techniques that exploit secondary, fluorescent radiation include microprobe analysis and particle-induced X-ray emission (PIXE). The physical process of XRF itself is non-destructive, and leaves the sample safe to handle. In many laboratory settings, however, samples are first ground to a fine powder and formed into pellets, or disks, in order to homogenize the sample and produce a clean, flat surface for analysis.

There are two primary branches of XRF technology. Wavelength-dispersive XRF (WDXRF) employs a crystal diffraction device to direct the secondary, fluorescent radiation toward a detector. The angle of the crystal in relation to the detector can be controlled to identify specific wavelengths. Energy-dispersive XRF (EDXRF, but often just referred to as XRF) generally directs an X-ray beam directly toward a sample, then
measures fluorescent radiation as it scatters back toward the detector. Portable XRF devices, such as the one employed in this project, use the EDXRF process, so all remaining discussion of XRF will be in reference to this type of analysis. In light of Frahm and Doonan’s (2013) recent typological distinction between small, lab-based pXRF devices, and the truly handheld pXRF devices, roughly the shape and size of a large power drill, it is important to note right away that this project employs the latter (termed by the above authors ‘HHpXRF’). More details on the specific instrumentation are provided below.

**Origins of XRF and use in archaeology**

XRF and its technological cousins became part of the archaeological toolkit in the decades following WWII, which in general saw an increased focus on physico-chemical analysis in archaeology (Pollard and Heron 2008:8). The physics of XRF, however, were well established by this point. The potential for using X-rays to chemically characterize materials was first realized in 1909, when Charles G. Barkla noted the relationship between the frequency of X-radiation emitting from an excited sample and the atomic weight of elements present (Shackley 2011:7). The earliest program to explore the use of XRF in archaeology occurred at Berkeley in the 1960s (Shackley 2011:11), and it has since become one of the most commonly-used geochemical techniques, particularly for lithic artifacts. The primary focus for users of XRF in the first few decades was overwhelmingly obsidian and other volcanic rocks, while the earliest ceramic geochemistry was generally conducted using neutron activation analysis (e.g., Sayre and Dodson 1957). NAA remains one of the most powerful and sensitive lab-based techniques, but requires access to a source of neutrons (i.e., a nuclear reactor).
Recent trends have altered this initial pattern. A recent bibliometric survey of archaeometric studies of ceramics (Poza et al. 2011) found that roughly an equal number of studies employed NAA and forms of XRF to study ceramics, and of these, the overwhelming majority were for characterization, as opposed to other technological inquiries. The survey showed a steady increase in ceramic geochemical and mineralogical research over the last decade. The majority of studies (59%) were focused on “Euro-Asian” cultures (Poza et al. 2011:190), a broad category, but largely reflecting the penchant for Mediterranean and Near-Eastern archaeologists to use ceramic provenance as a measure of interaction and trade in the Classical periods.

**Portable XRF: methodological revolution?**

Methodological innovation and rigorous assessment have always been integral in the field of archaeometry. Having historically partnered with colleagues in the physical sciences, archaeologists have long been engaged in the process of introducing new technology to the archaeological community and demonstrating its effectiveness for addressing topics of archaeological inquiry. A sign of a healthy scientific environment, each new generation of sophisticated tools has been met with a combination of enthusiasm, cautious acceptance, skepticism, and even rejection. At the moment of the writing of this project, an increasing number of researchers in the archaeometry community are engaged in such a deliberation (e.g., Frahm 2013b; Frahm and Doonan 2013; Shackley 2010; Speakman and Shackley 2013). The new technology seeking acceptance is handheld portable XRF.

Designed and manufactured for *in situ* elemental analysis, portable XRF analyzers saw initial use in scrapyards and other industrial sites, where rapid scrutiny of
alloys and ores can boost efficiency (Piorek 2008). The technology has also benefited industry and academic analysts interested in soil contamination (Ramsey 2008) and a range of other analytes. pXRF devices benefit from miniaturized instrumentation, highly sensitive detectors, and in most cases, non-radioactive X-ray sources (miniature X-ray tubes), which allow them to be transported easily across political boundaries, and to be used by non-specialist technicians (Liritzis and Zacharias 2011). Generally powerful enough to measure quantities of major, minor, and trace elements, portable analyzers are also efficient enough to run on batteries or AC power. Current generation analyzers are often equipped with tripods for in situ analysis, lab stands and automated sample changers for lab-based benchtop analysis, and removable PDA devices to store and review spectral data in the field. Many come with software that allows for easy manipulation and exploration of raw data and integration with geographic information systems (GIS). pXRF analyzers are commonly touted for their non-destructive analytical capability, making them popular with art historians, museum curators, and field archaeologists alike. These features have caused pXRF technology to surge in popularity within archaeology in the last decade; indeed, competing pXRF vendors are now commonplace at most major archaeological conferences (Shackley 2010). The primary distinction, and what for some may constitute a “paradigm shift” (Frahm and Doonan 2013), is the ability to take the spectrometer to the sample, rather than the other way around (Potts and West 2008:v).

The most obvious cases where the flexible and non-destructive capabilities of pXRF have been advantageous have been in museums, art galleries, and anywhere else where fragile or rare heritage objects reside (Liritzis and Zacharias 2011; Ridolfi 2012; Sciutto et al. 2012). In archaeological field settings, pXRF has been employed in
analyzing sediments associated with metallurgy, surveying for organic content in soil to
determine areas of past human activity, and in situ characterization of lithic raw materials
and many classes of artifacts subject to export restrictions (Frahm and Doonan 2013:1430). There is a sense that a field-based “chemical inventory” of artifacts could be
conducted as a component of the traditional sorting and categorizing that occurs, which I
discuss further in another section. An increasing number of archaeologists now regularly
employ pXRF in a laboratory setting as well, benefitting from its capacity for real-time
data manipulation and the flexibility of positioning archaeological samples against the
analytical window of the instrument (e.g., Reimer 2012; Sheppard et al. 2010).

Because of the major methodological differences between conventional XRF and
the new portable systems, an apparent majority of recent archaeological literature on
pXRF in recent years has comprised assessments, comparisons, and arguments for or
against its use of in various settings. A number of recent studies have assessed the
precision and accuracy of pXRF analysis in relation to more “powerful” techniques (i.e.,
able to detect a greater range of elements, and at lower levels) like neutron activation
analysis (NAA) and conventional XRF. Current-generation portable analyzers generally
have good “internal consistency” in their results (precision, or the capacity to provide
identical replicate results under the same conditions), making them useful for generating
compositional groups, but sometimes lack the accuracy required to compare absolute
data with more powerful techniques. When comparing pXRF with NAA in analyzing
Mimbres pottery, Speakman et al. (2011) found that while similar compositional groups
could be constructed, unambiguous separation between these groups remained
challenging with pXRF. The authors attribute this to the more powerful penetration
capacity of NAA, as well as the problem of bulk analysis of heterogeneous ceramics. I explore the latter issue further in the following section.

Goodale et al. (2012) compared two different pXRF systems with benchtop EDXRF, and found that while, for the most part, all three systems provided comparable results, the pXRF analyzers tended to mischaracterize certain elements, and revealed instrumental “drift” over time. I discuss instrumental drift in the experimental section of this thesis. These mirror earlier findings reported by Craig et al. (2007), who also found group consistency in Peruvian obsidians, but occasional differences in absolute elemental concentrations. The latter authors argue that this problem was easily avoided through calibration protocols, and posed no serious threat of erroneous interpretation. Nazaroff et al. (2010) report similar findings in comparing pXRF with conventional XRF and NAA. In all of these cases, distinct compositional groups were constructed using pXRF, but differences in power, sensitivity, and calibration made it difficult or impossible to compare the absolute numbers with those acquired by conventional techniques.

After testing pXRF against both conventional XRF and NAA for analyzing Mexican obsidians, Millhauser et al. (2011) found that none of the potential sources of error resulted in an inability to attribute artifacts to sources using pXRF. They report that artifact concavity resulted in reduced counts of certain elements, a phenomenon attributable to the distance between the window of the instrument and the artifact, which is well documented by several authors (e.g., Forster et al. 2011; Potts et al. 1997). Goren et al. (2011) found that pXRF, NAA, and optical mineralogy (OM) provided nearly identical results when used to characterize clay cuneiform tablets; they then confidently contributed absolute data acquired by pXRF on a previously unstudied group of tablets to a regional database.
Ellery Frahm (2012; 2013a; 2013b; Frahm and Doonan 2013; Frahm et al. 2013) has recently been engaged in methodological and theoretical integration of pXRF into archaeological practice. Some of this work has involved inter-instrumental and inter-technique testing such as that described above (e.g., Frahm et al. 2013), while other work explores the methodological and theoretical implications of this evolving technology (e.g., Frahm and Doonan 2013). The latter piece warns against making sweeping statements about the utility of pXRF, and anticipates that pXRF will see increasing use in a variety of innovative contexts, providing real-time data that could support or alter sampling, excavation, and artifact analysis strategies. Indeed, statistical methodologies have recently been proposed that would allow for in situ, real-time multivariate analysis of compositional data, further diminishing the role of the laboratory and its computational facilities (Sciutto et al. 2012). This has been likened this to a “paradigm shift” (Frahm and Doonan 2013:1432), a theoretical and methodological revolution which challenges the established authority of conventional XRF and NAA labs, and results in the development of approaches not thought possible before. Dramatic though it may sound, Ellery’s argument is both provocative and grounded in his own extensive exploration of in situ applications of pXRF. In this thesis, designed prior to Ellery’s recent publications, I make a similar argument based on laboratory analyses. While prone to certain types of error, pXRF technology will begin to “push the envelope” over the next decade, and I believe one way it will do that is by allowing us insight into ceramic compositional variability that was previously unavailable to archaeologists. I enlarge upon this later in the thesis.
Non-destructive testing: an analytical trade-off

A majority of high-powered analytical techniques rely on a form of sample preparation that usually results in partial or total destruction. NAA and lab-based XRF, for example, both generally require that the sample be crushed and formed into a homogenized pellet, in order to avoid a number of problems associated with sample morphology and chemical heterogeneity (often referred to as “bulk” analysis). This practice is perfectly acceptable in many cases; researchers will often send samples they can afford to “part with” (e.g., nondescript flakes or sherds) for destructive testing, and the data acquired will almost invariably result in a net gain for the research project. However, attention has been drawn to the importance of non-destructive testing, now available using a wide range of instrumentation. XRF and PIXE are both possible with minor sample preparation, as well as scanning electron microscopy (SEM) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Kuhn and Sempowski (2001) used non-destructive EDXRF and PIXE to analyze Iroquoian ceramic pipes from proto-historic Mohawk and Seneca sites in northern New York State. They found that the Mohawk compositional group entered Seneca territory between AD 1590-1605, a time which they propose marked the beginning of peaceful relations between the groups following the formation of the Iroquois Five Nations Confederacy, or League of Haudenosaunee.

This example of innovative ceramic research would not be possible using destructive methods, given the contemporary cultural importance of clay pipes to Haudenosaunee descendant groups. Similar cases are easily found in any field of archaeological research. There is a growing awareness among archaeologists and the
public about the nature of destructive testing of any form. It is in this political and methodological context that the current debate about pXRF technology is playing out.

What, then, are the disadvantages of non-destructive testing? There are several main factors at play, which are common to all non-destructive techniques, but sometimes amplified in the case of pXRF.

**Temper and heterogeneity**

Non-destructive techniques have been shown to be susceptible to sample heterogeneity, a particularly critical factor when dealing with ceramics, but equally important when analyzing coarse-grained lithic materials. Potts et al. (1997) explored the limitations of early-generation non-destructive pXRF analysis based on the mineralogy of silicate rock samples. Because X-radiation is attenuated by the mass of the sample, the depth of X-ray penetration (critical penetration depth) and volume of excitation were calculated, indicating the relatively small volume of sample contributing to the fluorescent signal. For several elements, Potts et al. found that up to 90% of the fluorescent signal originates from the first 10-15 μm of the sample, making it essentially a test of the composition of the surface. In addition, they found significant spatial variation in the intensity of detection across the 25 mm analytical window of the instrument. Excitation intensities were up to 10 times greater near the center of the window. They concluded that elements present near the center of the window will be over-represented in the raw data, a phenomenon that is amplified in coarser-grained samples (Potts et al. 1997:35).

Forster et al. (2011) came to similar conclusions in their assessment of current-generation pXRF for use with archaeological pottery. The analytical window of modern analyzers is much smaller (10 mm), but similar variation in detection intensity occurs; in
this case, several times more excitation occurs just off-center. Thus, an area of less than 5 mm$^2$ contributes disproportionately more to the fluorescent signal. The weighting of elements present in the sample is affected by their horizontal and vertical distribution within the excited volume of the sample. Forster et al. (2011) used replicate assays on rocks of varying grain size to determine the potential for error, finding that more replicate analyses were required on coarser-grained rocks like granite in order to effectively estimate the mean values of specific elements. This susceptibility to sample heterogeneity is an important factor to consider when pXRF is used on synthetic, heterogeneous materials like pottery.

In the Kuhn and Sempowski (2001) paper described above, the authors attempted to minimize the impact of large temper grains (as well as altered/eroded surfaces) by simply avoiding areas where more visible temper was present. In addition, they argued that the fine feldspar tempering material would not significantly impact the results, and indeed, it was possible for them to create distinct compositional groups. With pXRF it is difficult, but not impossible to avoid areas with a lot of temper. The problem of penetration depth remains, regardless of how the instrument is aimed at the sample. The XRF instrument used by Kuhn and Sempowski (2001) had a penetration depth of around 2-3 mm, meaning that any large temper grain immediately beneath the surface could still contribute to the fluorescent signal.

In light of my discussion in the second chapter concerning the transformations clays undergo on their journey to become ceramic objects, it is important to restate the main point. Even if it is possible to test an area “free” from temper, there are a multitude of other factors that will not necessarily be consistent from artifact to artifact, or vessel to vessel. Ultimately, the fine clay fraction of any ceramic piece is irreversibly altered. With
this in mind, the fluorescent contribution of temper seems like less of a source of error, and more an effect of sampling. Replicate analyses are one solution to this problem, whereby the mean concentration of elements in the sample, including those present in higher or lower amounts in the temper, is estimated to the researcher’s best ability.

Surface morphology and coatings

Forster et al. (2011) also study the impact of variable surface morphology on the efficacy of pXRF. Because X-rays are attenuated by air, any space between the analytical window of the instrument and the sample itself can diminish the intensity of excitation and fluorescence. The ideal condition is a smooth, flat surface that meets the window of the instrument easily. The reality, however, is that most artifacts that archaeologists are interested in analyzing (lithic flakes, ceramic sherds) are not smooth and flat. Forster et al. (2011) noted a significant decrease in elemental values when experimental samples presented a concave surface. The effect was disproportionately significant for some elements, such as Si and Ca. Experimental matrices that were etched at various degrees, perhaps simulating the effects of incised decorations on pottery, also saw a decrease in values for all elements. A similar pattern was reported for experimental specimens with organic surface coatings (blood, oil, glue, mylar sheeting).

These attenuation effects, along with the problem of sample heterogeneity, can be mitigated though “best practices”; choosing clean, flat surfaces whenever possible, avoiding areas with clear evidence of post-depositional weathering or leaching (although this may not always be visible), are all easy and sensible ways to minimize erroneous results. However, when pXRF was used to characterize an assemblage of Chalcolithic ceramics, Forster et al. (2011) were able to construct the same discrete compositional
groups, regardless of sample preparation. In other words, the overwhelming patterning of the compositional data acquired using pXRF negated the potentially confounding impacts of known and unforeseen factors. Frahm (2013a) recently made a similar assessment of pXRF for use with small, irregularly shaped obsidian flakes, conducting his analysis in intentionally “sub-optimal” conditions. His analyses remained almost 100% consistent, despite the presence of concavities and even surface debris.

**Analytical contingencies and instrument “drift”**

One major potential source of analytical error is human error. With many instrumental settings governing power and other variables, simple mistakes are possible. On another level, however, is the issue of instrument drift, an issue recently discussed by Frahm (2013a). All other things being equal, environmental, mechanical, and electronic parameters will still vary over time, meaning that analyses performed with identical settings a month apart still have the potential to give slightly different results (Frahm 2013a:168). This is an issue primarily affecting precision, or the ability to provide multiple identical results. Acknowledging this as an inevitability, archaeometrist have long used geological standards to track instrument performance over time. In practice, this generally amounts to performing a repeat analysis on a sample of known absolute elemental values (available through agencies such as the National Institute of Standards and Technology [NIST]), after every 5, 10, or 20 analyses on research samples. The results of these standard tests will show whether instrument drift, contamination, or other phenomena are impacting the precision of analysis over time.
Summary: two levels of variability

The pattern that has emerged in the literature presented here is that pXRF performs variably under differing analytical conditions, and when used on samples of varying physical properties. However, when applied to a substantial sample of artifacts, or when used to perform replicate analyses of a single sample, pXRF is rarely unable to generate data that can be used to construct viable compositional groupings (sensu Millhauser et al. 2011). An important argument made by most archaeologists currently employing pXRF is that it is not sufficient to use in isolation; rather, pairing it with other, more powerful techniques is a potentially fruitful research strategy.

More important than the actual technical abilities of all of these techniques is the philosophy behind their use. A field archaeologist with a tight budget will not send 500 flakes of chert to NAA lab for analysis (upwards of $200/sample). Instead, the archaeologist might opt to screen, or inventory, the 500 flakes using a rapid technique such as pXRF, to identify samples that warrant further testing. In cases where an argument for transport or migration hinges on the demonstration of a single exotic artifact, perhaps pXRF is not the best tool for the job. As the experimental component of this thesis demonstrates, however, this technology does provide certain advantages that make up for its occasional analytical shortcomings.

This chapter has made clear the variability that can exist within a single sample, particularly a ceramic artifact. The previous chapter, in which I discussed natural and cultural sources of ceramic variability, outlined the reasons why whole ceramic vessels will differ chemically from one another, even if they are constructed from similar raw materials. What archaeometrists are faced with, then, are two levels of variability: variability within an artifact, and variability across an entire ceramic assemblage. It is
obvious that an inadequate sampling strategy could result in erroneous interpretations of the ceramic technological organization at an archaeological site. For all of the criticisms levied against pXRF technology and its use in archaeological research, one arena in which it might truly shine is in investigating ceramic compositional variability. In the next chapter, I outline the rationale and methodology for the experimental component of this thesis, in which I explore the functionality of pXRF and the composition of ceramics in tandem.
Chapter 4 Repeatability study

Introduction

Methodological and theoretical debates in archaeological provenance hinge on the central concepts of precision and accuracy; researchers must know whether or not similar or identical results can be achieved repeatedly, using different techniques (precision), and whether or not those results come close to the actual levels (accuracy), in order to have confidence in their raw material associations. In the preceding chapters I have outlined a theory of ceramic composition, as well as a theory of portable X-ray fluorescence and its unique advantages and capabilities. This may engender in some a sense of uncertainty in the validity of the technique; exactly what is being measured during non-destructive pXRF analysis of archaeological ceramics? If ceramics are composed of a variety of unevenly distributed minerals, and pXRF is susceptible to sampling “error” when used to measure heterogeneous sample matrices, then to what extent does a single pXRF assay of a ceramic sherd represent the bulk geochemistry of the artifact? Questions such as this are best viewed from the perspective of precision, a term recently qualified by Frahm (2012:168) as having two distinct components: repeatability, “the agreement between sequential measurements under identical conditions”, and reproducibility, “agreement when observers, conditions, or instruments change or after time has passed”. In this study, I assess repeatability in measurement of elements in ceramics using pXRF.
Forster et al. (2011), following the methodology of Potts et al. (1997), have examined the repeatability of pXRF assays on a variety of lithic materials, including coarse-grained granite, by analyzing these matrices repeatedly at different locations and calculating the differences among the “shots”. This allowed these authors to demonstrate the relationship between increasing grain size in the granites and decreasing analytical precision. As the preceding theory of ceramic composition suggests, however, this approach does not effectively mirror the circumstances encountered when analyzing ceramics. Forster et al. (2011) proceeded to repeat this procedure on a small sample of Anatolian ceramics, but were limited in their interpretations by the size of their dataset. The present study uses repeat pXRF measurements of a larger sample of archaeological ceramics from varied sites to gauge variability among individual measurements, the first such study to view variability among several assemblages. Based on analyses by Forster et al. (2011) and Potts et al. (1997) on coarse-grained materials, we can expect variability related to grain size in non-destructive testing. This phenomenon, as it applies to ceramics, is also assessed qualitatively in this study, by carrying out paired comparisons of coarse- and fine-grained sherds.

Finally, this study assesses the benefit/impact of partial destructive analysis of ceramics. Following the earlier discussion of variable surface morphology and post-depositional alterations that differentially impact the surface, it can by hypothesized that that sectioning, or slicing, ceramic sherds to reveal clean, flat surfaces, could be beneficial for pXRF analysis, reducing variability from matrix effects and increasing precision. Indeed, Forster et al. (2011) assessed the potential advantages of partial- and fully-destructive testing, although again their small sample size limits the interpretive
strength of this assessment. Here I gauge the differences in analytical variability by sectioning the sherds using a diamond saw, analyzing the “core” surfaces, and reporting any patterned change from the exterior surfaces of these sherds.

This chapter first outlines the methodology, sampling, and instrumentation employed for this research. A short description of the data transformation and statistical procedures is included. The results are then presented, followed by interpretations and implications for pXRF ceramic research.

**Hypotheses**

Three areas of interest are noted in the preceding introduction: (a) the degree of variability among individual assays of ceramic sherds; (b) whether sherds that contain relatively coarser temper grains will reflect greater variability; and (c) whether or not partial-destructive testing impacts this variability. These components are re-formulated as hypotheses, and addressed in the following order in the results section below:

a) It is hypothesized that different elements will reflect greater or less variability between assays as a function of their relative concentration and distribution in the ceramic matrix (i.e. their presence or absence in the various mineral grains used to temper the raw clay). It is further hypothesized that repeat assays of ceramic sherds will reflect significant geochemical variability within individual artifact samples.

b) It is hypothesized that coarser-grained or more visually heterogeneous samples will be associated with greater variability between assays.

c) It is hypothesized that partial-destructive testing (sectioning) will result in greater precision (less variability between assays), but will also reveal differences between the surfaces and cores of the artifacts that relate to post-depositional alteration, the presence of slips or other surface coatings, or other matrix effects.
Materials and methods

Sample set

The ceramics used for this study derive from five archaeological assemblages in geologically and culturally distinct contexts.

The first two assemblages come from mid-sequence deposits at the Sigatoka Sand Dunes site, on the Coral Coast of the main island of Viti Levu, Fiji. The site has been a focus of Fijian archaeology for decades, and has received renewed attention from Burley and colleagues in the last decade and a half (Burley 2005; Burley and Connaughton 2010; Burley and Dickinson 2004). Two sets of ten sherds were sampled, deriving from two stratigraphically sealed deposits representing the Fijian Plainware (ca. 2300-1500 cal. BP) and Navatu (ca. 1500-1000 cal. BP) periods of Fijian prehistory. These Sigatoka midsequence sherds form the basis of a case study presented in the next chapter, and are discussed in greater detail at that point. The third Fijian ceramic assemblage is a collection of early Lapita (ca. 3000 cal. BP) sherds from Kavewa, an offshore islet on the north coast of Vanua Levu, Fiji. The sherds were collected during test excavation by Burley with my assistance in the summer of 2012. The fourth sampled ceramic assemblage was from the early Lapita site of Nukuleka, a large village site that represents the first landfall and settlement of Tongatapu, the principal island of Tonga. This site has been studied extensively by Burley and colleagues (Burley and Dickinson 2001, 2010; Burley et al. 2010; Burley et al. 2012). The fifth and final ceramic assemblage comes from Sevilla la Nueva, Jamaica, one of the first permanent European settlements in the New World. Burley and colleagues have recently investigated Sevilla la Nueva, and have recovered an assemblage of post-contact Taino earthenware ceramics (e.g., Woodward 2006).
**Experimental procedures**

Ten sherds from each of the five assemblages were selected from SFU collections. The sherds were cleaned by gentle brushing using distilled water to remove adhering surface particles. Each sherd was then sectioned using a low-rpm diamond blade saw to reveal a clean, flat surface. Each of the sherds was analyzed using pXRF at six different locations on exterior surfaces, with an additional six measurements on the interior (core) surfaces, for a total of twelve measurements each. Eighteen elements were measured and, of these, seven were examined in detail (Si, Ca, Mn, Fe, Zn, Sr, and Zr). Mean concentration, standard deviation, and coefficient of variation were calculated for each (these calculations are described below). Variability was assessed between the original and sectioned surfaces of each sherd in order to gauge the impact of partial-destructive testing, and between samples with visually distinct temper types and grain sizes. After every ten assays, repeat analyses of two powdered geological standards were performed. Variability among assays of these geological standards provides a baseline of analytical precision of a pure, homogeneous sample unaffected by the various matrix effects.

**Instrumentation and analytical conditions**

All analyses were undertaken using the Bruker Tracer III-V+ housed at the Department of Archaeology Geochemistry lab at Simon Fraser University. This handheld, portable XRF instrument is equipped with a Rh X-ray tube, 13 μm Be detector window with a diameter (spot size) of 4 mm. The Tracer II-V+ uses a Si Drift Detector for light element sensitivity, and a vacuum pump was used throughout to minimize air attenuation. Analyses were conducted at 40 keV, without the use of filters. This so-called “lab rat” mode employs a broad-spectrum screening strategy for all elements present.
Clean, flat surfaces, free of any visible residues, were chosen whenever possible for analysis. In some cases, surface features such as calcium carbonate deposits were unavoidable; these features were allowed to contribute to elemental variability for the purpose of illustration. In each case efforts were made to present the surface of the sherd as closely to the window of the instrument as possible, which occasionally required improvised weighing or propping up of curved samples. Samples were subjected to the X-ray beam for a live count of 120 seconds. Preferred assay times vary between researchers and research programs, sometimes reaching three or even five minutes each; two minute assays were chosen after longer assays failed to result in significant differences in X-ray counts.

During analysis, the fluorescent signal passes from the detector to a digital pulse processor, then directly to a computer that displays it in spectral form. Raw X-ray counts are calculated from the area under each spectral peak using Bruker S1pXRF and ARTAX software. Varyingly referred to as “net peak areas” or “raw photon/X-ray counts” these numbers provide the quantitative basis for comparison between elements. Calibration of these data and conversion to parts-per-million (ppm) was not undertaken for this study.

**Description of statistical treatments and calculations**

All statistical examination of the elemental data in this study was conducted using Microsoft Excel, JMP 10.0, an open-access statistics platform provided by SAS Institute Inc., and PAST 2.13, an open-access statistics platform developed by Hammer and Harper.
Variability between individual assays was evaluated in two separate ways, by using coefficients of variation (CV), and by calculating the number of assays required to achieve various levels of relative error.

**Coefficient of variation**

Coefficient of variation is a normalized measure of dispersion, useful for comparing datasets with widely different means. In this case, CVs were calculated for diagnostic elements in each set of six repeated assays and used as a measure of variability. A higher CV is indicative of a higher level of variability. CV is calculated using the following formula:

$$CV = \left( \frac{\sigma}{\overline{x}} \right) 100$$

where

$\sigma$ = standard deviation

$\overline{x}$ = mean elemental concentration

For each of the select elements in the tables below, the median coefficient of variation is calculated for both the exterior and core surfaces as a way of gauging their relative variability. Median is used rather than mean, as it is a better indicator of central tendency in populations with extreme outliers.

**The “number of shots”**

For selected sherds, the number of replicate assays required to achieve 2% and 10% relative standard error (SE) were also calculated. Simply put, this “number of shots” test indicates the number of times a sample would need to be analyzed, and the elemental
concentrations averaged, in order to achieve that level of precision relative to the calculated mean. They were calculated as follows:

\[
    n = \left( \frac{100\sigma}{R\bar{x}} \right)^2
\]

where

- \( n \) = “number of shots” required
- \( \sigma \) = standard deviation
- \( \bar{x} \) = mean elemental concentration
- \( R \) = relative standard error (either 2% or 10%)

Apart from being an alternative indicator of relative variability, these “number of shots” calculations also provide a measure of logistical feasibility for pXRF analysis on ceramics. While it is impossible to perform true, bulk analysis of ceramics using pXRF, due to the shallow depth and low volume of excitation, the logic of repeat assays suggests that a close estimate can be made by establishing mean values for diagnostic elements. These simple calculations provide a useful estimate of how many repeat assays would be required to make these estimations.

**Results and discussion**

Over the course of this repeatability study, over 600 assays were performed. The full results of these assays are contained in Appendix A. For illustrative purposes, seven elements, including major, minor, and trace elements, were selected for comparison. Results from each of the five assemblages are presented below, including a brief
description of each sample set, summary tables reporting the mean values and CV for each of the selected elements, and biplots depicting the compositional dispersion of samples using diagnostic elements. The summary data for the two geological standards are presented first in order to establish a baseline of elemental variability in a pure, homogeneous substance.

**PART 1**

**Powdered geological standards**

Table 1 presents the mean values and coefficients of variation for seven selected elements in two powdered geological standards, CHA-2 and PER-1, both volcanic rock types. Both standards were developed and certified by the National Institute of Standards and Technology (NIST). Because the standards are, in theory, “pure”, and because they are finely powdered, many of the matrix effects discussed do not have an impact on analysis. Variability between assays, however, is still apparent from Table 1. CV values for Zn, for example, are relatively high: 14 for the CHA-2 standard and 33 for the Per-1 standard. Variability in Si is also relatively high, especially given its higher

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**Table 1. Median concentration and CV of selected elements for repeat assays of two powdered geological standards. Values are presented in raw photon counts. As the data are not calibrated to ppm, published values of these standards are not employed here for comparison.**
concentration in the powder matrices. This variability is attributable to three separate phenomena.

The first phenomenon is air attenuation. Both standards are represented by roughly 15 mm of powder in a plastic sample cup, with ultra-thin mylar sheeting forming the bottom of the cup. It is through this membrane that the primary X-ray bombardment and fluorescent radiation passes; this is standard practice in XRF laboratories and it is agreed that the membrane has little to no attenuative effects. The powder, however, is not tightly packed; any air between the particles results in slight attenuation of X-rays. In nuclear-based bulk analytical techniques such as NAA, samples are pelletized to avoid this issue.

The second phenomenon contributing to variability in the geological standards is described by Forster et al. (2011) as “low peak-to-background” or “signal-to-noise” ratio, referring to the relatively low concentration of certain elements and their consequent higher variability. Forster et al. (2011) noted substantial increases in variability in elements present under 500 counts. This pattern is evident in the Zn column in Table 1. In general a pattern should emerge in the repeat assay data in which elements that are present in greater concentrations vary less than elements present in lesser amounts.

In addition to these two variables, lighter elements present challenges for low-powered analytical techniques. In this study, the elements Ca and Si appear to vary more widely than other elements. This may be attributable, in part, to their lower atomic mass. In Table 1, Si appears to contradict the expected pattern of high concentration-low variability. This is most likely a result of the light element effect – a known issue for pXRF analysis, as lighter elements are more attenuated by air (Forster et al. 2011).
The purpose of elaborating on the causes of elemental variability in these geological standards is to establish a baseline of expected variability in analysis to compare with the ceramic results. These powdered standards represent the closest to “ideal” analytical conditions possible, removing the potentialities of variable surface morphology, matrix heterogeneity and coarseness, and other matrix effects. Importantly, the three phenomena described above also act upon the ceramics described below. Although not powdered, many of the ceramics contain voids that could contribute to air attenuation; the effects of low peak-to-background ratio and the harder to measure light elements apply equally to the ceramic samples. In summary, elemental variability is expected, even when efforts are made to mitigate confounding variables. This is an important perspective from which to view the fluctuations in elemental variability in the ceramics below.

**Assemblage 1: Sigatoka Fijian Plainware**

**Depositional environment:** Coastal (sand dune near major river, mouth, no lagoon or fringing reef), 70-90 cm below surface.

**Colour:** Sherds range from yellow-brown (sherds 1, 2, 3) to reddish orange (sherds 4, 5, 6, 7, 8, 10) to deep red (sherd 9). Sherd colours are consistent between exterior and interior vessel surfaces apart from sherd 10, which displays a grey-black interior vessel surface.

**Texture:** Surface textures are smooth, with little to no surface cracking or pitting. No voids/vacuoles are observed. All sherds have a smooth, dense interior texture, apart from sherd 9, which has a looser, chalkier texture.
Temper type(s): Tempers are largely composed of fine to medium iron-rich and quartz-based sands, as well as mica (black flecks) with several examples of unusually large temper grains (sherds 1, 2, 3, 10). All sherds appear to contain trace amounts of fine calcareous sand (fine white flecks).

Surface coatings: No slips or post-depositional coatings are apparent.

Other observations: none.

Table 2 displays the mean concentration of select elements for each of the ten Fijian Plainware sherds, as well as a coefficient of variation calculated using the formula described above. Each entry is paired, with the bold numbers indicating results from the sectioned surfaces of the sherds. The bottom row displays a calculated median value of CVs for each element, as an indicator of relative overall variability in that element.

The substantial differences between the exterior and sectioned surfaces of the sherds become apparent in this table. This pattern is consistent across all five of the sampled assemblages, with values of certain elements fluctuating widely depending on the location of analysis. The relative degree of variability (as indicated by the median CV values) is also fairly consistent for these elements across the five assemblages.

The majority of elements follow a pattern of reduced variability (i.e. greater precision) on the sectioned surfaces, with the exception of Fe, and, more notably, Zn. An increase in the variability of Zn with sectioning is a pattern mirrored in all but one of the five assemblages sampled. One possible explanation for this trend is that Zn is more highly associated with raw clays than it is with mineral and calcareous temper sands. Unless the exterior surface of a sherd is wind-ablated or otherwise eroded, there tend
### Table 2. Median and CV of select elements in Fijian Plainware assemblage.

Bolded numbers represent assays of sectioned sherds. Each set of unsectioned and sectioned values represents six individual assays, performed at different locations on the samples.

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<th>Fe CV</th>
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<th>Mn CV</th>
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Median CV

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...to be fewer visible temper grains than in the sectioned interiors. Logically, therefore, more clay than temper is represented when an assay is conducted on the exterior surface. The increased concentration and precision of Zn at the surface would appear to indicate its relationship to clays rather than tempers, which dilute the presence of Zn in the interior.
Figure 3. Biplot of Si and Sr for the Fijian Plainware assemblage. Each colour represents an individual sherd, with each set of six open circles representing sectioned sherds and each set of six filled circles representing the exterior surfaces.

The differences between exterior and sectioned surfaces are further illustrated in Figure 3, a biplot of mean concentrations of Si and Sr for all 12 assays on each of the ten Plainware sherds. While the exterior and the sectioned surfaces of each sherd tend to cluster well respectively, the clusters are often fairly separated in compositional space, giving the erroneous impression of separate “compositional groups” as defined in chapter 2. In some cases dispersion within each cluster is similar (e.g., dark green circles bottom center), and in other cases, sectioned surfaces appear more dispersed (e.g., grey circles top center). The most extreme example is the sherd depicted in brown.
The exterior surfaces of this sherd cluster tightly together, but are distant from the corresponding cluster representing the sectioned surfaces. As noted in the description above, no slips or organic or mineral surface coatings were apparent on any of these sherds, which means the differences between interiors and exteriors are directly related to the distribution of minerals within the clay matrix.

In this assemblage and in the Navatu assemblage below, Sr remains fairly consistent regardless of the location of analysis. This trend is important to note, as it applies directly to the case study presented in Chapter 5.

**Assemblage 2: Sigatoka Navatu**

**Depositional environment:** Coastal (sand dune near major river mouth, no lagoon or fringing reef), 0-30 cm below surface.

**Colour:** Sherds range from dark grey-brown (sherds 8 and 9) to reddish brown (sherds 4, 5, 6, 7) to deep red (sherds 1 and 3) and reddish-orange (sherd 2). Interior vessel surfaces are generally dark brown to black. The majority appear differentially oxidized/reduced in profile (red exterior vessel surface, black interior vessel surface).

**Texture:** Exterior surfaces are smooth, with occasional minor cracks and pits. Sherds 2, 4, 5, and 6 exhibit voids/vacuoles in the interior and at the surface, the result of firing or erosion.

**Temper type(s):** All sherds contain a mixture of calcareous and mineral sands, the latter apparently comprising iron-rich and quartz-based sands. Temper grains are fine to medium, with no apparent examples of large grains.
Surface coatings: No slips or post-depositional coatings are apparent. Sherd 4 has organic residue adhering to the interior vessel surface (avoided during analysis).

Other observations: Several samples derive from smaller vessels and therefore display greater curvature. These samples were propped/weighted during analysis to ensure maximum contact with analytical window of the pXRF instrument.

Table 3. Median and CV of select elements in Navatu assemblage. Bolded numbers represent assays of sectioned sherds. Sherd 10 omitted for technical reasons.

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<th>Fe Mean</th>
<th>Fe CV</th>
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The Navatu assemblage was recovered from the upper levels of the same excavation units as the Fijian Plainware assemblage, representing an abandonment and subsequent reoccupation of the Sigatoka dune site. It is thought that the raw materials
used in the manufacturing of the Fijian Plainware and Navatu ceramics are likely similar, particularly the raw clay used. These assemblages are described in greater detail in the case study presented in Chapter 5.

Variability across the elements for Fijian Plainware and Navatu is fairly similar, with the notable increase in variability in Zr in the Navatu assemblage. The Zn pattern described above is once more apparent. The trend of increased precision with sectioning is contradicted slightly by Mn and Zr, both of which increase in variability by one CV value. Ca is equivalent between exterior and sectioned surfaces, but fluctuates widely among individual sherds. This is likely related to the differential distribution of calcareous tempers in this assemblage. Because these artifacts were recovered closer to the surface, the possibility also exists that Ca concentrations were impacted by post-depositional alteration/weathering.

The biplot in Figure 4 depicts the relationship between Mn and Zn. The biplot reveals an interesting pattern, in which sherds appear to resemble each other more closely when sectioned than when not sectioned. Most notable is the decrease in Zn levels when sherds are sectioned, a pattern evident in other elements as well (e.g., Ti, see appendix). The significant increase in Si on the sectioned surfaces (Table 3) suggests its association with the quartz grains that comprise the temper sands, a pattern explored further below.
Figure 4. Biplot of Mn and Zn for the Navatu assemblage. Each colour represents an individual sherd, with each set of six open circles representing sectioned sherds and each set of six filled circles representing the exterior surfaces.

Assemblage 3: Vorovoro

Depositional environment: Coastal (beachfront facing barrier reef), 35-40 cm below surface.

Colour: Colours range from yellow-brown (sherds 3, 4, 6) to orange-brown (sherds 1, 2, 9) to dark reddish brown (sherds 2, 7, 8, 10). Several display differential oxidation in profile (sherds 3, 5, 9, 10).
**Texture:** Textures range from smooth and hard (sherds 3, 9) to rougher and crumbly (the remainder). All sherds display long, horizontal voids/air pockets in profile, apparently related to initial vessel construction.

**Temper type(s):** Sherds 1, 3, 5, and 9 contain medium to large calcareous temper grains, with a minority of iron-rich and/or quartz-based mineral sands. Variability in grain size is particularly apparent in sherds 1 and 5. Sherds 2, 4, 6, 7, 8, and 10 contain medium to large iron-rich and quartz-based mineral sands, to the exclusion of calcareous temper. Several (including sherds 4 and 10) contain examples of unusually large iron-rich sand grains.

**Surface coatings:** The majority (sherds 1, 2, 5, 6, 7, 9, 10) display a thin and patchy calcareous surface deposit, likely related to their coastal depositional environment.

**Other observations:** A diversity of thicknesses is suggestive of several different vessel types being represented in this sample set. All sherds are relatively small and in a general poor state of preservation, likely related to the air pockets.

The magnitude and variability of elements in the Vorovoro assemblage is similar to the first two Fijian assemblages, with the notable increase in the concentration of, and variability in, Ca. This is doubtless related to the minor but prevalent calcareous deposits on the surfaces of the sherds, left in place to illustrate this very phenomenon. Despite the potential for these coatings to introduce error, variability in most elements is similar or even less than in the Sigatoka assemblages. This is also despite the presence of
Table 4.  **Median and CV of select elements in the Vorovoro assemblage.**
*Bolded numbers represent assays of sectioned sherds.*

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Large air pockets in most sherds, a factor which should, in theory, introduce air attenuation and decrease precision. The surface-exterior differences are less marked in some sherds, as illustrated in Figure 5, but are still present. Sherds in this assemblage are more readily distinguishable on a chemical basis, which was expected, given the presence of several visibly distinguishable paste types containing distinct temper suites.
Assemblage 4: Nukuleka

Depositional environment: Coastal (sheltered lagoon), 105-115 cm below surface.

Colour: Colours range from dark brownish red (sherds 2, 3, 7, 8) to deep red (sherds 4, 6, 9, 10) to reddish orange (sherds 1, 5). All display differential oxidation in profile.

Texture: Textures range from smooth and hard (sherd 1), to chalky (sherd 5), to looser and crumbly (the remainder).
Temper type(s): Tempers are dominated by fine to coarse ferrous grains, with small amounts of fine calcareous temper in sherds 2, 4, 6, and 9. Temper grain size in these sherds is highly variable, with several examples of unusually large ferrous temper grains. Sherd 1 is an exception, containing almost entirely fine-grained calcareous temper, with a small amount of mineral sands present.

Surface coatings: Sherds 2, 3, and 8 may have a slip applied to the exterior surface; appears as a thin dark reddish-brown layer in profile. All sherds possess to a small degree thin calcareous surface deposits.

Other observations: none.

Mineralogically, this assemblage is distinguished from the three Fijian assemblages primarily on the relative absence of calcareous temper, which appears in only small amounts in several of the sherds. The exception is sherd 1, which appears to contain almost exclusively calcareous temper, based on the dominance of white flecks and the absence of any darker grains in the paste matrix. Notably, sherd 1 does not show a consequent increase in the concentration of Ca; in fact, sherd 1 has the lowest Ca value of the ten sherds analyzed. This pattern suggests that higher levels of Ca may contributed by the non-calcareous mineral sands that make up the bulk of the Nukuleka tempers, than are contributed by the crushed shell and coral in the form of calcium carbonate. Ca could, in this case, derive from Ca-feldspars. Additionally, shell and coral-derived tempers may be more susceptible to post-depositional Ca leaching than rock-derived mineral grains (e.g., Dickinson and Nunn 2013).

The intuitive assumption that Ca should increase with the use of calcareous temper was also contradicted by the decrease in Ca in the Fijian Navatu assemblage,
Table 5. Median and CV of select elements in the Nukuleka assemblage. Bolded numbers represent assays of sectioned sherds.

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Several other patterns in the Nukuleka results are worth noting. Variability in Fe is fairly high, despite its high concentration. This may be interpreted as another example of the disruptive presence of variable calcareous deposits on the surface; indeed variability in Fe is significantly reduced in the sectioned assays. The reduction in concentration of Fe in the interior of the samples is likely due to the increased
prevalence of lesser elements, a process of dilution that is evident in all the sampled assemblages.

Figure 6. Biplot of Sr and Zn for the Nukuleka assemblage. Each colour represents an individual sherd, with each set of six open circles representing sectioned sherds and each set of six filled circles representing the exterior surfaces.

Similar improvements in the precision of Si and Sr measurement are noted; Sr in particular shows a sharp increase in concentration when sherds are sectioned, as illustrated in Figure 6. The Nukuleka assemblage is the only sample set to display this trend, as Sr remains fairly consistent in the other four sets. Importantly, while several
Nukuleka sherds have what appears to be an intentional slip, all ten sherds reveal a similar pattern of Sr reduction at the surface. Whether this relates to the ceramic technology itself or to post-depositional alteration is difficult to interpret. In their focused study of post-depositional alteration in "corroded" Aegean ceramics, Schwedt et al. (2004) found significant reductions of Ca, Cs, Rb, K, and Na (the latter four are alkali metals) at the surface of their sherds when compared to drilled core samples. The authors interpreted this as strong evidence for diagenesis, and their case is convincing. The study, however, sampled only artifacts deemed “corroded” based on seemingly subjective visual inspection, and included no control group of better-preserved samples. The strong pattern of change in elemental concentrations in this study, exemplified by the increase in Sr in the Nukuleka sherds, suggests there may be fundamental technological reasons for these differences. That systematic surface-core differences exist in all five of the sampled assemblages is convincing evidence that differential diagenesis is not the only factor at play.

**Assemblage 5: Sevilla la Nueva**

**Depositional environment:** Coastal (no lagoon or fringing reef)

**Colour:** Colours range from light brown (sherd 5), to reddish brown (sherds 2, 3, 9), to reddish orange (sherds 1, 4), to dark red (sherds 6, 7, 10). Sherds 2, 6, 7, 8, and 9 display differential oxidation in profile.

**Texture:** Textures are highly variable, from smooth and seemingly vitreous (sherds 2, 5, 7, 9), to coarse and crumbly (sherds 1, 4, 6, 10) and chalky (sherd 3).
Temper type(s): Tempers range from fine, quartz-based mineral sands (sherds 2, 3, 7, 8, 9, 10) to medium quartz and calcareous sands (sherds 1, 4) to highly variable mineral sands (sherds 5, 6).

Surface coatings: All sherds display at least minor calcareous surface coatings, with several (sherds 1, 3, 4, 7, 9) displaying thicker, calcareous encrustations. These coatings were left in place during analysis for illustrative purposes.

Other observations: High variability in paste texture suggests several distinct vessel types represented in this sample set.

Table 6. Median and CV of select elements in the Sevilla la Nueva assemblage. Bolded numbers represent assays of sectioned sherds.

<table>
<thead>
<tr>
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<th>Sr</th>
<th>Zn</th>
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<td>Mean</td>
<td>CV</td>
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Median CV

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<th>Zn</th>
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</table>
The defining characteristic of the Sevilla la Nueva assemblage is the degree of variability in Ca on the exterior surfaces, which drops dramatically in the sectioned assays. For example, sherd 7 has a Ca CV value of 106 on its exterior surface, which drops to 2 when the sherd is sectioned. The full table of results (appendix A) shows that Ca raw photon values for this sherd range from 15112 to 97807 on the exterior surface, giving the set of six exterior surface measurements a standard deviation exceeding its mean. This is, without doubt, due to the substantial calcareous surface deposits visible on the exterior of the

![Biplot of Sr and Zn for the Sevilla la Nueva assemblage. Each colour represents an individual sherd, with each set of six open circles representing sectioned sherds and each set of six filled circles representing the exterior surfaces.](image)

*Figure 7.* Biplot of Sr and Zn for the Sevilla la Nueva assemblage. Each colour represents an individual sherd, with each set of six open circles representing sectioned sherds and each set of six filled circles representing the exterior surfaces.
sherds. Both the degree of calcareous deposition and the variability of Ca increased dramatically from the Nukuleka assemblage, which contained sherds with minor traces of calcareous coatings. This pattern was expected, and is useful to demonstrate for reasons impacting the creation of “best practices” protocol, discussed more below.

Other than Ca, changes in the concentration and variability of elements followed similar patterns to the other sampled assemblages. The decrease in precision of Zn measurement is pronounced in the Sevilla la Nueva assemblage, with a jump from a median CV value of 13 on the exterior surface to 27 on the sectioned surfaces.

Figure 7, which plots Sr against Zn for the Sevilla la Nueva assemblage, shows the dramatic shift in Zn values when sherds are sectioned, almost tripling in some cases. Sr values, however, remain fairly consistent (a stark contrast to the Nukuleka results), and instead serve as useful diagnostic indicators of paste differentiation. Using Sr values alone, clear distinctions can be made between groups of sherds that relate to each other chemically, likely the result of similar raw material ingredients and amounts being used. In a larger sample, such differentiation would eventually lead to the identification of cohesive clusters of datapoints, each one denoting an individual paste recipe. Importantly, these diagnostic elements are not universal; Sr is a strong diagnostic element for Sevilla la Nueva, but not for Nukuleka or the Sigatoka assemblages. As the biplots above have demonstrated, different elements must be selected to illustrate different phenomena in each individual assemblage sampled.
PART 2

“Number of shots” calculations

Following Forster et al. (2011), Table 7 shows the estimated calculations, based on the formula described above, of how many repeated assays would be required to achieve certain levels of precision for different elements in five randomly chosen samples.

Table 7. Number of assays required to achieve 10% and 2% relative standard error (SE) for select elements, using five sampled sherds as examples. Bolded numbers represent assays of sectioned sherds.

<table>
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<td>10%</td>
<td>2%</td>
<td>10%</td>
<td>2%</td>
<td>10%</td>
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The overall patterns are similar to those demonstrated through the calculations of coefficients of variation; however, these results are more illuminating from the perspective of laboratory protocol. As this study has demonstrated, the selection of “diagnostic” elements tends to assemblage-specific, and requires exploratory compositional analysis. Table 7 indicates one measure of usefulness of each of the select elements, as well as an idea of how precise the measurements are expected to be in heterogeneous samples. Fundamentally, these results indicate that repeat assays can be necessary in order to acquire a mean measurement with good precision.
If the analyst is satisfied with achieving 10% SE for select elements, then in general, fewer than five repeat assays are required. As I argue below, attempts to achieve precision at the level of 2% SE are potentially misguided and not useful. Apart from Fe and Si, two of the most abundant elements present in these assemblages, few elements can be measured at that level of precision using any less than 7 or 8 repeat assays. A program of ceramic research using 8 repeat assays, at 2-3 minutes per assay, for each sample, is arguably redundant and inefficient. As demonstrated in the case study in Chapter 5, using single or dual assays, on a great many more samples, is infinitely more informative than attempting to secure absolute measurements of each trace element of interest.

PART 3

Grain size and variability

Quantitative data regarding the shape, density, and size of temper particle grains within ceramic matrices are within the purview of in-depth mineralogical analyses. Braun (1982) demonstrated the utility of x-radiography for more rapid measurement of densities and size grades in experimental specimens, but both methods are nonetheless outside the scope of this thesis. While grain sizes are strictly defined under several classification schemes, archaeologists generally use the descriptors “fine” and “coarse subjectively in their typological schemes. The range of grain sizes present in a clay matrix can be highly variable (poorly-sorted), making classification difficult.

Forster et al. (2011) reported a relative increase in elemental variability in lithic samples (basalts) described on an unnamed scale of “very fine” to “medium” grain size.
The present study similarly contrasts relative fineness of temper grain size in order to carry out paired comparisons of sherds from each of the five sampled assemblages.

Two sherds from each of the five assemblages were selected based on their contrastive relative grain size, based on visual inspection of their sectioned surfaces. The Fligner-Killeen test of homogeneity of variances was used to evaluate the relationship between grain size and elemental variability. This test provides a means for establishing whether variance is consistent among independent populations. The test was chosen for its conservativeness and resistance to outliers and non-normally distributed data. The null hypothesis is that variance is equal in both populations; the Fligner-Killeen test provides a $p$ value that can either reject or not reject the null hypothesis ($p \leq 0.05$). The minor element Mn was chosen as a proxy for overall variability. Mn measurements for each of the six assays on the sectioned surfaces of the sherds were used for the test.

As the results below indicate, the null hypothesis was not rejected once, despite the seeming disparity between coefficients of variation. Because the Fligner-Killeen test measures homogeneity based on the median, rather than the mean of each population, it is more resistant to outliers than is CV, which is calculated using mean. While CV remains a useful tool for viewing relative variability over a large dataset, these paired tests indicate that the increase in variability is not always statistically significant.

Another factor influencing these results was the subjective sampling method. Samples were chosen based on visual inspection of temper properties.
Figure 8. *Plainware fine-grained (sherd 6) and coarse-grained (sherd 10) samples.*

**Table 8. Fligner-Killeen test of homogeneity of variances for Mn in Plainware sherds.**

<table>
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Figure 9.  *Navatu fine-grained (sherd 2) and coarse-grained (sherd 6) samples.*

Table 9.  *Fligner-Killeen test of homogeneity of variances for Mn in Navatu sherds.*

<table>
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**Figure 10.** Vorovoro fine-grained (sherd 7) and coarse-grained (sherd 8) samples.

**Table 10.** Fligner-Killeen test of homogeneity of variances for Mn in Vorovoro sherds.

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Figure 11. *Nukuleka fine-grained (sherd 1) and coarse-grained (sherd 7) samples.*

Table 11. *Fligner-Killeen test of homogeneity of variances for Mn in Nukuleka sherds.*

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<td></td>
</tr>
<tr>
<td>1232</td>
<td>3088</td>
<td></td>
</tr>
<tr>
<td><strong>CV</strong></td>
<td>44</td>
<td>10</td>
</tr>
<tr>
<td>Fligner-Killeen <em>p</em> value</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Null Hypothesis rejected</td>
<td>no</td>
<td></td>
</tr>
</tbody>
</table>
Figure 12. Sevilla la Nueva fine-grained (sherd 7) and coarse-grained (sherd 5) samples.

Table 12. Fligner-Killeen test of homogeneity of variances for Mn in Sevilla la Nueva sherds.

<table>
<thead>
<tr>
<th>SEVILLA LA NUEVA</th>
<th>Fine (sherd 7)</th>
<th>Coarse (sherd 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2154</td>
<td>4420</td>
<td></td>
</tr>
<tr>
<td>2086</td>
<td>2786</td>
<td></td>
</tr>
<tr>
<td>1917</td>
<td>2283</td>
<td></td>
</tr>
<tr>
<td>1615</td>
<td>2791</td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>3482</td>
<td></td>
</tr>
<tr>
<td>1357</td>
<td>2048</td>
<td></td>
</tr>
<tr>
<td>CV</td>
<td>20</td>
<td>29</td>
</tr>
<tr>
<td>Fligner-Killeen p value</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Null Hypothesis rejected</td>
<td>no</td>
<td></td>
</tr>
</tbody>
</table>

Although the null hypothesis that variance between sherds was uniform is not rejected, a general pattern of relative CV increase can be seen in each assemblage but one (the CV of sherd 1 in the Nukuleka assemblage was influenced by an outlier). The pattern of increased variability may not be quantifiably demonstrable using the present dataset, but a general pattern is apparent. This may be an important consideration when developing laboratory protocols for use with particularly heavy-tempered, coarse-grained ceramics.
Summary and conclusion

This investigation of repeatability in pXRF assays of ceramics has highlighted a number of important phenomena with the potential to impact non-destructive compositional analysis of archaeological ceramics. While some phenomena act at the level of the assemblage, and may be mitigated through sample preparation (e.g., calcareous surface deposits are easily removed using a mild acidic solution), there are other, more universal patterns that have emerged.

At a fundamental level, the study has demonstrated that significant variability can exist between individual assays of the same ceramic artifact. On the exterior surfaces alone, without sectioning, variability in measurement of specific elements can result in “erroneous” generation of separate compositional clusters. The importance of this basic fact cannot be understated, given how subtle the geochemical differences may be between technologically distinct ceramics (see case study presented in chapter 5).

Partial-destructive analysis can offer increased precision, but this benefit is not universal, and should not be taken at face value. This approach suffers at a theoretical level from its ignorance of total compositional variability in ceramic artifacts, and the potentially relevant data encoded therein. This study has highlighted several distinct and consistent patterns of elemental change between the exterior surfaces of the artifacts, and the theoretically “unaltered” interior surfaces when sectioned. As alluded to above, these patterned changes cannot be explained by weathering or leaching alone. Indeed, the parsimonious explanation is that technological variables, dictating the distribution of
minerals and their constituent elements within the paste matrix, are ultimately responsible for this seemingly universal pattern. Importantly, the elements that shift in concentration and variability are not universal across each assemblage.

The intuitive benefits of attempting to access portions of an artifact that have not undergone reductive or absorptive environmental change is part of the larger mindset of the “lithic paradigm” of geochemical sourcing; that is, the inappropriate application of the principles of sourcing obsidian, which is a molecular “solid”, to porous, synthetic ceramic items. An integral concept in the debates surrounding the precision, accuracy, and validity of differential instrumental techniques is the theoretically flawed search for elemental “truth”. For an individual obsidian flow, there may indeed be one true and absolute constellation of trace elements, which allow for accurate and predictable source assignment. However this study, and others, have shown that when it comes to ceramics, there may be several such “truths”. Whether the exterior surface or the sectioned interior comes close to what an obsidian analyst would define as “accuracy” is itself subjective, depending on what the ceramic analyst wishes to learn about the object being measured.

Moreover, the idea of destructive analysis misses the point, to a degree, of using technology such as handheld pXRF in the first place. The argument could be made that all samples should be crushed and pelletized, as is standard practice with techniques such as NAA. This would certainly eliminate variables such as surface morphology, grain size, heterogeneity, and air attenuation. However, such efforts would amount to a misguided attempt to replicate the analytical capabilities of NAA using low-powered XRF. Instead of exploiting the advantages of pXRF, such a strategy attempts to mitigate its deficiencies. Well-informed choice of instrumental techniques is, of course, essential.
Pelletizing also removes a layer of relevant data: if the surface of the artifact is vastly
different from its interior, who is to say that blending the two in pellet form will bring the
sample any closer to analytical “truth”?

Partial-destructive and non-destructive analysis are equally valid in their own
regard; that is, different phenomena are measured with equal validity. But the two
strategies are not directly comparable. Any research program employing non-destructive
analysis of ceramic artifacts should bear in mind the compositional differences that can
exist within a single sample, and make efforts not to combine fresh breaks with
weathered surfaces.

Another important conclusion of this study is that some elements are good
indicators of variability, and some are good diagnostics – but that these elements are not
universal and must be established for each new assemblage using exploratory tests. A
small-scale repeat assay study such as the ones presented here is useful in this regard.

Regarding specific elements chosen for analysis, several statements can be
made. Ca was found to be one of the most variable elements, but importantly, this was
attributable to different factors that were sample- or assemblage-specific. The most
obvious factor impacting Ca variability was the presence of calcareous surface deposits,
which varied in magnitude across the sampled assemblages and produced predictable
increases in Ca mean concentration and CV. Ca values will obviously fluctuate with the
distribution of calcareous tempers; however, it was found mineral tempers can contribute
higher levels of Ca than the less durable shell- and coral-derived calcareous sands. This
was exemplified by sherd 1 at Nukuleka, the only one dominated by calcareous temper,
but nevertheless displaying a lower Ca level than the rest of the dominantly mineral
sand-tempered sherds. This pattern was also demonstrated in the two Sigatoka assemblages; the Navatu assemblage, despite having greater quantities of calcareous temper, showed an overall lower value of Ca than did the Fijian Plainware sherds.

Importantly, Ca fluctuates even in the powdered geological standards presented above, indicating that its relatively light atomic mass presents a challenge for low-powered XRF analysis. In addition, Ca has been found in other contexts to be impacted disproportionately by weathering. Ogburn et al. (2013) found in their study of stone construction materials that long-term weathering disproportionately affected light elements, particularly Ca. Heavier elements, such as the "mid-Z" elements commonly used in sourcing (e.g., Mn, Fe, Zn, Y, Zr), were unaffected. Ca may be particularly susceptible to dissolution in certain environments, an idea recently posited by Dickinson and Nunn (2013) to explain the presence of grain-sized vacuoles on the surfaces of Fijian Lapita sherds excavated several kilometers northwest of Sigatoka on the Rove Peninsula. The vacuoles or voids present on the surface and in the interior of some sherds may alternatively represent "blowouts", or pock-marks, from superheated calcareous grains exploding during firing. Rye (1976:120) describes the chemical basis for this phenomenon: calcium carbonate (CaCO₃) decomposes to calcium oxide (CaO) and carbon dioxide (CO₂) when heated. CaO can combine with water vapour (H₂O) to create calcium hydroxide (Ca(OH)₂), which occupies more volume than CaO. This reaction can lead to fractures, or, in the case of a controlled and intentional firing regime, simply leave pock-marks at the surface where the reaction occurs more readily. As Rye (1976) explains, calcareous tempers are still preferred by potters in certain regions, owing to their other functional properties, despite this one functional drawback. Whether or not Ca becomes more active during firing or in the millennia between deposition and
recovery, all of these factors combine to make Ca an inherently complex and potentially problematic element to use for certain aspects of compositional analysis. But while its usefulness for sourcing, in the traditional sense, may be jeopardized, its applicability to diagenesis studies, and others, remains important.

Major elements such as Fe and Si tend to vary less, owing to their greater concentration, but are nonetheless equally impacted by surface-core differences. Their distribution at the surface and in the interior may be roughly equal, but are proportionately more or less represented in analysis due to the presence or absence of diluents; an increase in the amount of Zn at the surface of a sherd will result in an equal, proportional decrease in the Fe, at least hypothetically. This concept becomes important in the interpretation of case study results in chapter 5.

Zn remained the only element to increase almost universally in concentration at the surface, increasing in many cases by over 50%. One possible explanation for this is the greater association of Zn with raw clays than with tempers. It may be proportionately better represented at the surface because of the relative decrease in large, visible temper grains. Alternatively, the relative consistency of Sr in both Sigatoka assemblages could also indicate an association with clay, as it remains unaffected by the increased prevalence of temper beneath the surface. Both explanations make intuitive sense, and may not be mutually exclusive. Further investigation of this phenomenon is required before conclusive statements on its origin can be made.
Protocol and “best practices”

Recent calls have been made for the development and observation of strict laboratory protocols (e.g., Shackley 2010; Speakman and Shackley 2013). This emphasis makes sense, and indeed lab protocols are both useful and necessary if reliability and standardized research are the desired outcomes. These authors are concerned, for the most part, with obsidian sourcing, an endeavour that can benefit from the generation of regional databases. This position has recently been challenged by Frahm (2013a, 2013b), who argues from a theoretical perspective that sourcing is not, in the strictest sense, geochemistry, it is, rather, a form of archaeological typology (2013b:1445). An over-emphasis on analytical performance, in Frahm’s view, misses the mark, and equates validity of a technique not with its ability to distinguish raw materials and assign artifacts to them, but with the ability to generate “true” results in an objective sense. Nonetheless, the present study provides evidence for variability in pXRF measurement, and from that body of evidence, guidelines emerge that can help define best practices for non-destructive analysis of ceramics.

First and foremost, as the results above have shown, interior/core assays and those conducted on the exterior surface of a sample are not directly comparable. Whatever sample preparation method is used must be applied consistently. This requires prior knowledge of the nature of the sample set, as the state of preservation of the ceramics may dictate whether sectioning, abrading, crushing, or other destructive measures are required.

Exploratory measurements on a small, representative sample should be standard practice at the outset of a ceramic compositional research program. Before instrumental settings and sampling strategies are decided, one must have an understanding of
variability in the sample set, particularly as it applies to “diagnostic” elements. This should be accomplished using broad-spectrum, “lab-rat” settings that screen for all elements present. While the general ratio of major to minor and trace elements appears relatively stable in earthenware ceramics, significant deviations from this pattern are important to note from the outset.

As has been stated elsewhere (e.g., Forster et al. 2011), proximity and angle of the specimen in relation to the instrument window are important. In this study, individual specimens occasionally required weighting or propping in order to face the instrument window in perpendicular fashion. Cleaning and other measures are, of course, vital in order to eliminate contamination from the adhering sediments. In cases where calcareous surface deposits exist, as in the Nukuleka and Sevilla la Nueva assemblages, a mild solution of acetic acid (vinegar) and water is sufficient to remove them. It must be stated, however, that any erosive or corrosive cleaning regimen has the potential to remove soluble elements from the ceramic matrix itself (Cogswell et al. 1998); calcareous encrustations are not totally reversible in their impact on ceramic composition. They may, for better or worse, need to be considered part of the “total artifact”; the theory of ceramic composition outlined in earlier chapters acknowledges the necessity to view each variable as equally contributing to a total mineralogical and chemical configuration, and points out the theoretical flaws in attempting to recover or synthesize the unaltered specimen.

**Geochemistry versus geochemical inventory**

This parsing of analytical precision crosses paths with a larger discussion of utility and validity of instrumental techniques, with one major variable being the selection of an
appropriate tool for answering the research questions at hand. As argued above, pXRF cannot and should not be expected to perform bulk analysis with the same convincing power as NAA and other major instrumental techniques. To attempt this is to miss the point. As was pointed out repeatedly during special symposia at the recent 2013 Annual Meeting of the Society for American Archaeology (e.g., Frahm 2013c; Goodman-Elgar 2013), pXRF technology should be used in a way that exploits its unique advantages: rapidity, non-destructive capability, and of course, portability, to name a few. When used on ceramics or other heterogeneous sample matrices, it should be acknowledged that assays represent an averaging of matrix constituents.

I have argued that a “lithic paradigm”, with all the trappings of finely-tuned and calibrated obsidian studies, is not always appropriate for ceramic research. With increasing access to “user-friendly” analytical technology such as pXRF, and with renewed interest in geochemistry as a tool for studying ceramic technology and provenance, a separate set of principles must be developed and adhered to. Any ceramic compositional analysis, whether destructive or non-destructive, must go hand-in-hand with a theory of ceramic composition that acknowledges the myriad cultural and environmental factors influencing the concentration of minerals and their constituent elements within the ceramic matrix.

Without doubt, the primary advantage of pXRF in a laboratory setting is the speed of analysis and the ability to generate results in real-time. In this thesis, I have covered a range of theory that gives a sense of the compositional variability that can exist within and between ceramic vessels; the experimental component has demonstrated the variability that can exist within a single sherd. While not equivalent to NAA in terms of accuracy or detection limits, pXRF may in fact be better suited for
investigating broader-spectrum technological aspects of ceramic technology, simply owing the speed and repeatability of analysis. Hypothetically, in a scenario involving a ceramic analyst and a large assemblage of sherds, the analyst could choose to sample a small number and send them to an NAA lab for high-powered analysis. The results would include highly accurate values for several dozen major, minor, and trace elements. Alternatively, the analyst could choose to examine a much larger sample using an “inventory”-style program of rapid pXRF assays. The latter, I argue, has the potential to be more informative to the analyst – a larger sample could reveal compositional patterning affirming or contradicting stylistic or chronological associations.

To characterize this fundamental distinction in strategies as a difference in research philosophy is not an overstatement. Under the lithic paradigm, analysts use powerful machines and strictly-defined protocol to produce results that accurately characterize the true and total geochemistry of an artifact. Under the alternative theory of ceramic composition, in which variability is understood to be natural, and both behaviourally and environmentally relevant, a more widespread investigation using rapid techniques to identify and isolate foreign paste recipes is more appropriate. It is in the unnecessary collision of these two research philosophies that the unfortunate debate about the utility of pXRF and other techniques is currently waged.

Through the experimental component of this thesis, I have sought to evaluate the utility of pXRF by reframing the question – by assessing pXRF on its own terms, and by understanding how the technique behaves in relation to ceramics. In a list of questions that one should ask when selecting an instrumental technique for analysis, Rice (1987:374) asked: “Is accuracy required, or is precision sufficient?” The present study has taken the question of precision a step further by examining the results of sequential
measurements from the perspective of repeatability. The results reflect the level of compositional variability that is expected in synthetic, anthropogenic sample matrices.

In Chapter 5 of this thesis, I present an inventory-style analysis of archaeological ceramics on a relatively small scale, using the two Sigatoka assemblages sampled above as a case study.
Chapter 5: Case study: Fijian mid-sequence ceramics from the Sigatoka Sand Dunes

Introduction

A case study applying non-destructive pXRF to archaeological ceramics was conducted using an expanded sample of sherds from the Fijian Plainware and Navatu components of the Sigatoka Sand Dunes site. This chapter outlines the rationale, methods, and results of this case study, concluding with a discussion of its relevance to the major themes of the thesis.

The results of the repeatability study presented in Chapter 4 helped to inform a view of ceramic compositional variability that is directly relevant to non-destructive analysis. Considerable variability occurred between individual pXRF “shots”; this variability was largely attributed to mineralogical heterogeneity and other matrix variables, rather than instrument “performance”. While each assemblage presented a unique set of circumstances, several universal trends emerged, most notably, the consistent geochemical differences between the external surfaces of the samples and their sectioned, interior surfaces.

In the discussion of these results, it was argued that pXRF technology is uniquely suited to investigations of ceramic composition that differ fundamentally from traditional lithic studies that rely on the comparability of absolute data between observers and instruments. In a discussion of instrument validity, Frahm (2012:171) probes the concept
of validity by asking, “... does an analytical technique, when combined with data analysis, discern raw-material sources (i.e., geochemical groups) and assign artifacts to them?” The implied message of this query is that even in cases where instruments are incapable of producing absolute data comparable with bulk techniques such as NAA, their utility as archaeological tools is not necessarily impacted.

In chapter 4, I considered ceramic compositional variability at the level of the artifact; in the present chapter compositional variability is explored at the level of the assemblage. The driving question of this component of the thesis is this: Is rapid, non-destructive pXRF analysis a valid tool for investigating technological organization of ceramics? Put another way, can pXRF analysis contribute to an understanding of technology and chronology by characterizing ceramic paste recipes? The results presented below demonstrate that an inventory-style approach can reveal culturally-significant patterning in compositional variability, and that pXRF has utility and validity extending beyond “sourcing” in the traditional sense.

**Archaeological context: the Sigatoka Sand Dunes**

The Sigatoka River rises in the western highlands of Viti Levu, the principal island of the Fiji group, and empties into the ocean on its southwest coast. The Sigatoka Sand Dunes are a system of parabolic dunes beginning at its southern extent, where the river empties into the ocean, and extending some 5 km northwest. Sediments carried out to sea by the river are washed onto this shoreline and blown by the persistent northeasterly winds up the slopes of these dunes, which can reach up to 60 m in height (Burley 2005).
The Sigatoka Dunes have been an important locus of archaeological investigations in Fiji since the 1940s (Dickinson 1998) and they continue to be investigated to the present (Burley 2005; Marshall et al. 2000). Stratified deposits continually erode from the windward sides of the dunes, exposing abundant ceramics and other evidence of periodic habitation at the mouth of the Sigatoka River.

The Dunes have been revisited several times in the last decade and a half by Burley (2005; Burley and Connaughton 2010; Burley and Dickinson 2004). Excavations have focused on expanding a previously excavated area at the eastern end of the dunes with stratified deposits representing superimposed but stratigraphically separated village occupations. The two primary “living floors” are alternatively associated with the Navatu Phase (ca. 1500-1000 cal BP) and the Fijian Plainware Phase (ca. 2300-1500 cal BP). These phases together form what is known as the Fijian mid-sequence, and are stratigraphically separated at Sigatoka by a sand layer of variable thickness. Underlying the mid-sequence deposits at Sigatoka are “level 1” or Late Lapita materials (ca. 2700-2450 cal BP). Burley (2005) has argued that the Fijian Plainware ceramics evolved directly from Late Lapita, forming a tradition of ceramic continuity from the earliest settlement of Fiji to approximately 1400 cal BP. Burley further argues that Navatu period ceramics represent a distinct and abrupt shift in ceramic technology, possibly the result of an incursion of Melanesian peoples and/or technologies (Burley 2005; Burley in press). The two occupations, which, at Sigatoka, occur less than a century apart, are easily distinguishable on the basis of decoration, vessel form, and mode of manufacture. The idea of a migration into Fiji at this time has been challenged by other researchers (e.g. Clark 2009), but it remains one viable explanation for the Plainware-Navatu “disjuncture” that is evident at Sigatoka.
The sherds used in this study are non-diagnostic sherds, meaning they are undecorated, and not part of a rim, neck, or collar. They derive from two 1 m² units, separated by several meters, excavated during the 2012 Simon Fraser University archaeological field school in Fiji. Both units had well-defined stratigraphy, showing no evidence of intrusion from upper levels into lower levels. Each of the assemblages comes from a well-defined living floor with stratigraphic integrity. Crucially, this supports the assumption that the plain, nondescript sherds sampled for this study can be compositionally analyzed based on their temporal provenience at the site.

**Hypothesis**

The Sigatoka Sand Dunes site occurs less than 300 m to the west of the present Sigatoka River mouth, and while no raw clays are available in the dunes themselves, plentiful raw clay sources are likely available in their immediate vicinity, within the delta/estuarine system. No systematic sampling of raw clays in the area has yet been conducted, but it is assumed that raw clays in this area are mineralogically and geochemically similar, given the primary depositional regime of the river. The archaeological occupations themselves reflect fairly small settlements, and it is unlikely that potters traveled any great distance to procure raw materials.

Having made these assumptions, I hypothesize that the Fijian Plainware and Navatu ceramics are geochemically similar (i.e., they will not reflect entirely distinct compositional groups). I predict, nevertheless, that the overall patterning will reveal distinctions between the two major groups, possibly reflecting changes in the selection and/or addition of tempering agents. Navatu vessels are distinguishable from Fijian Plainware ceramics by a variety of stylistic and morphological features. For Navatu, one
of the latter is a greater use of calcareous tempers (Burley 2005), a shift that should be reflected in geochemical composition. I further hypothesize that smaller compositional clusters will emerge, reflecting other morphological changes in production, groups of similar vessels made as a “batch” by a single potter using the same clay/temper, and/or distinct paste types/recipes.

Importantly, this exploratory study is not “blind”; stratigraphic control means that sherds were previously identified as either Fijian Plainware or Navatu. Rather, it is meant as test for differences between the assemblages, and an assessment of a pXRF inventory strategy for investigating technological change in the archaeological record. It also provides additional insight into the distinctiveness of Navatu and Plainware ceramic suites. Following the discussion in Chapter 4, this case study does not represent “sourcing” in the strictest sense, but rather a form of XRF-based typology. Future environmental sampling of raw clays in the vicinity of the dunes would contribute to the interpretation of the results presented below.

**Materials and methods**

All ceramic sherds from the two units greater than 3 cm in length were sampled for analysis. In total, 326 sherds met this description, including 166 Fijina Plaiwnare sherds and 160 Navatu sherds. Many of the artifacts had adhering sediments and other residues from the field. All sherds were first dry brushed, then gently cleaned in distilled water to remove adhering particles. The choice of distilled water was made to avoid contamination by soluble elements present in tap water; it is acknowledged, however, that any cleaning regimen has potential to remove soluble elements from the fragile ceramic matrix. With this in mind, cleaning was conducted as gently and quickly as
possible. All sherds were left to dry over the period of a week so that excess moisture would not interfere with or attenuate X-rays.

A handful of sherds had burnt organic residues present on what would have been the inner surface of the vessel. These residues were largely left intact, and every attempt was made to avoid them during analysis (i.e., the outer surfaces were analyzed). In addition to the ceramic sherds, one raw clay sample recovered from the Navatu occupation floor was included in the analysis. The clay was powdered and analyzed several times by pXRF to achieve mean compositional values, and included in the statistical analyses.

The analytical procedure and instrumentation used for the repeatability study in Chapter 4 was used again on this larger sample. A single assay was conducted for each individual sherd, and raw X-ray count data were recorded for a number of elements. A powdered geological standard was measured after every ten assays to assess instrument stability.

Raw elemental data were transformed using a base-10 logarithm (log10). This has recently been recommended by Baxter and Freestone (2006), who argue that log10 transformation redistributes variables with long-tailed distributions, making them more symmetrical and therefore better for graphical representation. Additionally, each variable is represented at a similar order of magnitude, which is beneficial for statistical analysis, particularly the multivariate techniques used and described below. This is particularly important when exploring the relationships between elements that are present in widely dissimilar amounts (for example, Fe may have a raw photon count above 25,000, while Rb, an important trace element, is present in the order of less than 1000).
Description of statistical techniques

At a fundamental level, statistics are used in compositional analysis to identify the inter-correlation among several variables at once, in this case, elements. Orton et al. (1993:184) note that compositional data are complex and often require the intervention of data analysis procedures. In the past, raw spectral data, particularly for obsidian sources, were often compared visually for differences and similarities. Today, however, most geochemistry labs employ quantitative or semi-quantitative data, often comparing several elements at one time. This study employs both bivariate and multivariate strategies for illustrating the structure of the elemental data. All statistical analyses in this thesis were conducted using the statistical software packages JMP 10.0 and PAST 2.13, as well as Microsoft Excel.

In many cases, the relationship between two elements can yield clear separation between samples of differing geochemistries. It is common to graphically depict the relationship between elements in “compositional space”, including simple bivariate analysis. Biplots depict the relationship between two diagnostic elements, often trace elements, and usually with the intention of maximizing difference between compositional groups. Multivariate statistics are used more frequently for ceramics, owing to their great compositional variability and the need for a test that can consider many variables at once. As the repeatability study showed, different elements vary in different proportions depending on the location of analysis – multivariate treatment of elemental concentrations, therefore, may help to mitigate the impacts of diagenesis and the various matrix effects (Gallelo et al. 2013). While biplots are good for maximizing group identification, principal components analysis (PCA) might be better for revealing the
natural internal structure of the groups (i.e., more reflective of overall compositional reality).

Principal components analysis was used in this study to assess the internal structure of the geochemical dataset. PCA is a dimension-reduction technique that transforms a large number of variables (in this case, elemental concentrations) into a smaller number of more manageable components. It is an exploratory technique that expresses data in a way that highlights similarities and differences – useful for identifying compositional groups in elemental data. PCA was applied to the data generated in this study to visually inspect the total chemical distinction between the two assemblages. It has been recommended that only diagnostic, structure-carrying variables be included in multivariate statistical tests such as PCA (described below), as variables that are not structure-carrying can hamper the ability to detect structure (Baxter and Freestone 2006:524; Michelaki and Hancock 2011).

Discriminant function analysis (DFA) is another multivariate dimension-reduction technique, which, at a basic level, is a test of the differences between groups. Using the assemblage category (Fijian Plainware or Navatu) as a “predictor” variable, DFA maximizes the differences between the two groups and categorizes them accordingly. The success of the variable as a predictor is reflected in the percentage of individual data points that are accurately categorized based on the available data. This is useful when data groups are known a priori (in this case, clear stratigraphic separation of Fijian Plainware and Navatu sherds made their categorical distinction robust).
Results

In total, 326 individual sherds were analyzed by pXRF. Concentrations of Al, As, Ca, Cr, Cu, Fe, Ga, K, Mn, Nb, P, Rb, Sc, Si, Sr, Ti, V, Y, Zn, and Zr were measured during analysis.

Figure 13. Biplot of log10-transformed Mn and Zn for the expanded Sigatoka sample set. Blue dots are Fijian Plainware sherds, green dots are Navatu sherds.

Figure 13 illustrates the relationship between Mn and Zn for the total Sigatoka sample set, two highly diagnostic elements that maximize group distinction in bivariate
compositional space. The Fijian Plainware (blue dots) and Navatu (green dots) assemblages form distinct compositional clusters, with some overlap. As hypothesized, the datapoints appear to reflect geochemically distinct, yet similar, ceramic paste regimes.

**Figure 14.** Biplot of principal components analysis. Component 1 accounts of 36.2% of variance in the dataset; component 2 accounts for 20.9%, for a total of 57.1% of variance accounted for. Correlation matrix for this PCA is in appendix B. Blue dots are Fijian Plainware sherds, green dots are Navatu sherds, black dots are a powdered geological standard. The red dot is a raw clay sample, described below.
Figure 14 plots the results of a PCA test of the dataset, this time including the results of repeat assays of the powdered geological standard (black dots). This PCA considers variability in Ca, Cu, Fe, Mn, Si, Sr, Ti, V, Zn, and Zr. The result is the generation of two clusters, similar to that in Figure 13, but with increased overlap. As described above, this multivariate relationship better reflects the overall internal structure of the dataset, revealing both similarities and differences between the Fijian Plainware and Navatu assemblages.

The variability reflected in the powdered geological standard gives an indication of baseline variability. The minimal dispersion of these datapoints could reflect a degree of instrumental drift, unavoidable fluctuations in electrical current, atmosphere, and other variables. This sort of drift was expected, given that the analyses took place over a period of several weeks, interspersed by periods when other researchers were using the instrument.

The bivariate and multivariate plots above follow closely the expectations of Arnold’s model of “hierarchical” or “nested” compositional variability (Arnold et al. 1991), where specific assemblages are compositionally related in a regional sense, but have an extra level of distinction, or source attribution. The patterning of the Sigatoka sherds appears to reflect a shared use of clay sources, which is expected given the overwhelming tendency for Fijian ceramics to be composed of locally available materials. There are, however, two distinct regimes of pottery production at work, which could differ in terms of temper selection and addition, clay cleaning and preparation, vessel use, deposition, or a combination of factors. While post-depositional alteration and other factors have been discussed as a possible source of variability, it is likely that the bulk of the separation between these compositional groups is “behaviourally
relevant”; that is, the patterning reflects, to some degree, conscious choices about pottery-building made by informed artisans. Even subtle modification of the paste template (i.e., ratio of clay to temper) could explain these compositional differences. The reasons for these technological choices, and the differences between Fijian Plainware and Navatu potters, would require a level of scrutiny that is beyond the scope of this research. However, this exercise demonstrates the potential of the geochemical inventory strategy as a platform for investigating technological organization and spatial and temporal change.

With a greater sample size, it is anticipated that the patterning would increase in complexity, revealing clusters that represented categories or sub-categories of vessel types. The inclusion of other sites that are geographically and/or geologically related to the Sigatoka excavations, will provide a regional profile of ceramic pastes. The relationships between Fijian Plainware and Navatu could then be examined at a greater scale.

Upon visual inspection of the sherds using their composition as a guide, it is clear that the compositional patterning does tend to reflect visually similar pastes in the artifacts themselves. While much of this could simply mean the sherds originated from the same vessel, particularly given the fact that only two 1m² units were sampled, several cases of chemically similar sherds originating in different excavation units exist.

**Ca and calcareous temper**

As described above, Navatu ceramic pastes are generally distinguishable by their greater incorporation of calcareous tempers, which are derived from crushed shell and coral. As the repeatability study in Chapter 4 suggested, an increase in calcareous
temper does not necessarily result in an increase in Ca. Indeed, the results of this expanded sample of Sigatoka sherds further supports this idea.

Figure 15 depicts Ca levels in the Navatu and Fijian Plainware assemblages. While the Plainware sherds display higher overall variability in Ca, they also have a

Figure 15. Box plot with concentrations of Ca for Fijian Plainware and Navatu assemblages.
significantly greater mean concentration of Ca than the Navatu sherds. These results further suggest that Ca can be more concentrated in mineral sands (as well as clay minerals) than in calcareous tempers; the intuitive assumption that shell tempers will result in higher Ca is not always appropriate.

**Raw clay analysis**

The red dot in Figure 14 represents the single powdered raw clay sample included in the analysis. The sample was included in the analysis in order to explore its relationship with the pottery, and to find support for the hypothesis that it represents the raw clay actually used by the site’s inhabitants to manufacture pottery. While the clay sample differs greatly from the ceramic sample in its concentration of several elements (see Table 5.1), the configuration of elements used in the PCA plot (Figure 14) positions the clay sample centrally relative to the ceramic assemblages. This means it falls within the range of variability of the ceramic assemblage when the elements Ca, Cu, Fe, Mn, Si, Sr, Ti, V, Zn, and Zr are combined.

**Table 13. Mean concentration of select elements in the raw clay sample and in the total Sigatoka assemblage.**

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Sr</th>
<th>Zn</th>
<th>Zr</th>
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</thead>
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<tr>
<td>raw clay sample</td>
<td>6730</td>
<td>412620</td>
<td>5637</td>
<td>6298</td>
<td>1554</td>
<td>649</td>
<td>1450</td>
</tr>
<tr>
<td>mean value of Sigatoka sherds</td>
<td>10171</td>
<td>321422</td>
<td>1865</td>
<td>11370</td>
<td>1883</td>
<td>590</td>
<td>1497</td>
</tr>
</tbody>
</table>

Table 13 displays elemental values for the raw clay sample and overall mean values for the Sigatoka ceramics. While the values of Sr, Zn, and Zr are similar, Ca, Fe, Mn, and Si are distinct. Further scrutiny of these elements reveals one possible
explanation that allows for these distinctions, while still demonstrating that the clay is mineralogically related to the sherds.

Of the three elements that differ little between the raw clay and the sherds, Sr is unique. In the repeatability study presented in Chapter 4, Sr levels remained consistent throughout the repeat assays, regardless of where they were performed (exterior vs. interior). This suggested early on that Sr might be more strongly associated with the clay rather than tempers, as its value fluctuated little even with tempers present. That the Sr value in the raw clay is so similar to the sherds would tend to support this hypothesis, if the clay were indeed confirmed as the raw source material.

Inspection of the major elements reveals a pattern of expected discrepancy; raw clays should not, after all, be geochemically identical to finished ceramic vessels. The raw clay shows a relatively higher Fe level, which would, in fact, be expected in an Fe-rich clay that has not yet been diluted by temper sands. The raw clay also has a lower Si content, which is also expected, given that none of the Si-rich temper sands have been added yet to enrich Si in the paste.

This hypothesized relationship requires further examination in order to make an objective source attribution. While this explanation is only one of several possible explanations, it provides an example of the level of scrutiny required in making source attributions in ceramic provenance research.

**Geochemistry as excavation tool**

Discriminant function analysis (DFA) was undertaken on the dataset to determine the degree of separation between Fijian Plainware and Navatu sherds. DFA is a dimension-
A reduction technique that maximizes the differences between multivariate datasets to create variables (functions) that predict group membership of individual datapoints.

Figure 16 displays the results of the DFA. The success of classification using the assemblage as a predictor was 94.5%, meaning that in almost all cases, Fijian

Figure 16. Discriminant function analysis of Sigatoka sherds. Assemblage category (Fijian Plainware vs. Navatu) successfully predicts group membership 94.5% of the time.
Plainware and Navatu sherds are geochemically distinct. Their group “membership” is easily predictable using the multivariate matrix available.

The significance of this test is twofold. First, it indicates that despite inherent error and/or variability in non-destructive analysis, enough “good” data exist in the inventory to make meaningful conclusions based on the separation of these two groups in compositional space. In other words, the patterning made apparent in the PCA and bivariate Mn-Zn plots above is made more “legitimate” with the strengthening of the Fijian Plainware-Navatu dichotomy. The more “real” these groups are (i.e., they are not stratigraphically mixed), the more useful these compositional data become.

An extension of this logic is its application to the real-world context of excavation. In the case of the Sigatoka site, the director of excavations (Burley) identified a spatial zone where little or no mixing had occurred between Fijian Plainware and Navatu levels. This was confirmed by excavating in stratigraphically controlled spits and analyzing diagnostic rims and decorated sherds later in the lab. The compositional data presented here provide an additional level of confidence in this stratigraphic separation. In other words, the DFA shown above provides concrete evidence that all non-diagnostics recovered during excavations were indeed stratigraphically separate.

The use of real-time geochemical analysis to resolve stratigraphic questions is an intriguing line of inquiry. This strategy was recently been employed by Davis et al. (2012), who used pXRF assays of in situ archaeological soil samples to construct a chemo-stratigraphic profile. This allowed them to correlate artifacts with stratigraphic units from isolated points at the site, and independently evaluate the “tying in” of strata as they occurred in separate excavation units. The results of the DFA presented above
indicate that artifacts themselves are useful stratigraphic indicators; when analyzed in the field, they may provide useful guidance for excavation strategies, particularly in situations where visible stratigraphy is absent.

**Summary and conclusion**

Clear compositional separation of Fijian Plainware and Navatu sherds was evident, with substantial overlap indicating a similarity in the types of raw materials used by potters in either tradition. It can be hypothesized that the potters used similar or identical clays, but different types and different amounts of temper. These ceramic “recipes” are likely intentional technological frameworks, shared between potters and passed on via knowledge transmission, that relate to the requirements of the finished ceramic vessels (functional, aesthetic, or otherwise). The compositional groups established using non-destructive pXRF analysis align well with the abrupt chronological shift (Fijian Plainware-Navatu boundary) that has been proposed for the site (e.g., Burley 2005, 2013).

Importantly, and despite the potential for error inherent in non-destructive compositional analysis of ceramics, the distribution of ceramic sherd datapoints in compositional space appears to reflect culturally/behaviourally-relevant patterning. Inspection of sherds that cluster in compositional space reveals groups of similar paste types that link the two 1 m² units.

From a logistical perspective, the establishment of a high-resolution geochemical survey of ceramics from Sigatoka was relatively simple and not overly time-consuming. Larger inventories have been completed in the past, using more expensive and powerful techniques. Neff (1995) subjected some 2000 Guatemalan samples to NAA, with great
success for the interpretation of ceramic regimes in that region. However, the present study took a matter of weeks, with no research budget beyond the instrument, and no destruction of artifacts. In addition, it could, conceivably, have been conducted in a field setting, with a real-time impact on excavation. This opens a door for future excavation/analytical projects to incorporate broad-spectrum geochemical survey as a part of traditional cataloguing/accessioning procedures.

The potential for geochemical data to resolve stratigraphic issues was highlighted and discussed. In the case of Sigatoka, discriminant function analysis of all sherds showed an almost perfect classification rate, indicating the potential for geochemistry to attribute non-diagnostic sherds in mixed or unstratified deposits to analytically useful chronological units. From the perspective of the debate surrounding the nature and timing of the break between Fijian Plainware and Navatu ceramic regimes (e.g. Burley 2013), these data indicate that a substantive shift in ceramic technology occurred in the intervening time. Again, DFA solidifies the distinction between these assemblages.
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Appendices
Appendix A. Full results of repeat assays

Tables containing the full results of the repeat assays are available in PDF on a DVD enclosed in this thesis package.


**Appendix B. Correlation matrix for principal components analysis**

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<tr>
<th></th>
<th>Ca K12</th>
<th>Cu K12</th>
<th>Fe K12</th>
<th>Mn K12</th>
<th>Si K12</th>
<th>Sr K12</th>
<th>Ti K12</th>
<th>V K12</th>
<th>Zn K12</th>
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