The effects of ceramic manufacturing behaviour on identifying clay sources:

petrographic and chemical analyses of the modern Zulu ceramic production process

in the Thukela River Basin, South Africa

BY

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Abstract

This thesis aims to evaluate the compositional changes that occur when raw clays are transformed into finished vessels, and how these compositional changes impact provenance research. Petrographic and chemical techniques are used to analyse clays at each stage in the production sequence used by Zulu potters in KwaZulu-Natal, South Africa. The results of this research demonstrate that tempering behaviour, particularly the mixing of clays, can significantly alter the composition of ceramic vessels, depending on the ratio of clay types. The provenance of mixed clays and vessels can be determined when the range of variation between clay sources is known. Different ratios of constituent clays significantly affect the composition of finished vessels.

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Chapter 1. Introduction

The provenance of raw materials is a useful tool in archaeological research because it provides information about the production and distribution of material culture. Most classes of material culture display a certain amount of variability in composition or appearance, which allows archaeologists to associate artefacts with raw material sources. However, unlike homogeneous materials such as stone, the composition of ceramics can be altered by human behaviour. When a stone tool is manufactured, the geochemical composition of the rock does not change. When raw clays are processed, material may be added or removed, potentially altering the mineralogical and chemical composition of the clay.

The assumption behind ceramic provenance research is that "at no time during pottery manufacture…is the trace element configuration characteristic of a raw clay deposit significantly altered" (Rice 1978:514). In reality, there are a number of factors that may affect the compositional variability of ceramic vessels, including clay acquisition, processing and firing (Arnold 2000; Arnold, et al. 1991; Neff, et al. 1988). Pots produced using clay from the same sources do not necessarily have the same composition, due to the effects of clay selection, processing and firing. Although archaeologists are aware of the different factors that can influence ceramic composition, it is difficult to account for those factors in analysis. Insufficient research exists that documents how ceramic composition reflects cultural behaviours.

In order to better understand how behavioural factors affect ceramic composition, mineralogical and chemical analyses were undertaken for this thesis research using raw

and processed clay samples from each stage in an ethnographically documented production sequence used by Zulu potters in KwaZulu-Natal, South Africa. The relationship between particular processing stages and changes in clay composition was assessed to determine the effect of processing behaviour and its implications for provenance research, and to evaluate the potential for using compositional data to reconstruct processing behaviour.

Chapter 2 is a review of provenance research in archaeology, outlining some of the behavioural factors that can affect ceramic composition. These include resource procurement, clay processing, and firing of finished vessels. Provenance research involves examining the composition of sherds and vessels to determine the geographic or cultural origin of artefacts. Ceramic characterization techniques are discussed, including mineralogical and chemical approaches, as well as the strengths and weaknesses of different techniques. This is followed by an overview of provenance research in South Africa, which highlights key problems with previous research that need to be addressed. Based upon this review, I then present my research question and associated hypotheses.

Chapter 3 is a short description of the study area, followed by a discussion of the materials and methods used to collect data for this thesis. In Chapter 4, the results of mineralogical and chemical analyses are presented in order of processing stage. Chapter 5 discusses the compositional changes that can be observed as a result of processing behaviour, and whether provenance can be determined despite those changes. In the final chapter, Chapter 6, I discuss the implications that this research has for future provenance studies both in southern Africa and elsewhere, and I provide several suggestions for future research directions.

Chapter 2. Literature Review

Provenance research in archaeology is concerned with determining the origin of an artefact, either in geographic space or in terms of its culture of origin. Methods have been developed for determining the provenance of different classes of material culture, especially those produced by craft specialists working with stone, metal, or ceramics. Although these methods share many similarities, here we are concerned with ceramic material culture.

Ceramics have had great utility in archaeology due to their durability, stylistic variability and our ability to determine their geographic origin. Ceramics can provide evidence for trade, migration and other social interactions when their location of manufacture is known. Methods of determining the provenance of ceramic artefacts have made significant strides with the help of mineralogical and chemical techniques, as well as contributions from ethnoarchaeological studies of modern craftspeople. However, one of the most significant problems is relating these scientific data to the actual cultural behaviour of artisans (Arnold 2005:15).

2.1 Ceramic Provenance

Early attempts to determine the geographic origin of vessels were based on the spatial occurrence of pottery styles. Using the "criterion of relative abundance," archaeologists defined the zone of manufacture as the region where ceramics of a particular style occurred most frequently (Rice 1987:177). However, styles associated with different regions can be imitated or adopted in other areas, making them an

inconclusive indicator of geographic origin. A more effective method for determining the origin of ceramics was borrowed from the geological sciences, and uses mineralogical and chemical data to associate ceramics with their geographic origin.

The ability to determine the provenance of an artefact is based on the provenance postulate, which states that compositional variation *between* geological sources of raw materials is likely to be greater than variation *within* a source (Bishop, et al. 1982:301, italics mine). This assumption allows archaeologists to determine, with reasonable confidence, whether different artefacts were produced from the same source material, and to distinguish locally and non-locally produced artefacts. The provenance postulate was developed in geology, and takes into account the natural variation in raw materials, since this is the principal source of variation in rocks and minerals. This approach was easily borrowed by archaeologists studying lithic technology, since the manufacture of stone tools alters the form of raw materials, but not their composition. Fired ceramics resemble sedimentary rocks, in that they are a conglomeration of mineral inclusions in a fine paste. However, there are a variety of factors that influence ceramic composition besides natural variation.

2.2 Behavioural Factors and Composition

The large number of factors that produce variation in ceramics can be grouped into three classes: natural variability, procurement variables, and paste preparation variables (Arnold 2000). Natural variability in clays is influenced by local geology, erosion and depositional processes, and chemical alteration due to leaching. Unlike natural variability, procurement and preparation variables are a consequence of human cultural behaviour. Procurement variables include potters' selection of raw materials

based on the perceived quality and properties of clay and differential access to sources. Paste preparation variables include processing and tempering of clays, and mixing materials from different sources (Arnold 2000).

2.2.1 Resource Procurement

The basic raw material required for ceramic production is clay. Clay may be collected wet or dry, from individual or multiple sources. Depending on the characteristics of the clay, temper may also be required. A wide range of materials may be used to temper pottery, some of the most common being sand, shell, ash, and grog (ground potsherds) (Arnold, et al. 1991; Gosselain 2008b; Rice 1987). If the chosen temper material is not immediately available to the potter (as grog is), then its acquisition will be affected by the same factors that affect clay acquisition. Factors that relate to resource acquisition include procurement strategies and the different restrictions of access to sources.

The procurement strategies employed by potters fall into one of five categories: non-discriminating (potters use many clays and display no preference), discriminating (potters exploit a single preferred source), specializing (potters use several sources, each for different type of pottery), compounding (potters mix clays from different sources), and importing (potters use clay from distant sources) (Bishop, et al. 1982:317). These strategies will have different effects on the composition of ceramics. Non-discriminating, discriminating, specializing and importing strategies would be expected to produce ceramics whose composition is related to a single source, although in the case of importing, that source will be outside the potter's resource area. Compounding strategies

would be expected to produce ceramics that reflect a mixture of two or more compositional profiles.

Resource acquisition is also influenced by a number of possible restrictions that limit a potter's access to resources. Distance to resources is a fundamental factor that influences resource acquisition, and potters in sub-Saharan Africa tend to exploit clay within a three kilometre radius of their location of manufacture (Gosselain and Livingstone Smith 2005). Natural forces can also be a limiting factor, as when dry river beds become inundated during the rainy season. Access to resources may be limited by cultural or political factors, including land ownership and group membership (Arnold 1985, 2000; Bowser 2000). These restrictions can limit potters' access to preferable sources, changing their resource exploitation behaviour.

Complicating the application of the provenance postulate is the fact that compositional variation within a source may actually be quite significant. The term "source" is itself problematic, as it can refer to a single extraction site, a widespread clay stratum, or all the clays in a single drainage (Arnold, et al. 1991). At any of these levels, a source may exhibit a great deal of variation, or it may be extremely homogenous, and either scenario will affect the precision of provenance research.

2.2.2 Processing

Potters employ many different techniques to produce their end product: a viable pot. It is understood that those techniques have the potential to alter the composition of clay, making it more complicated to determine provenance (Carpenter and Feinman 1999; Neff, et al. 1988).

Raw clay is often ground into a fine powder, which is further refined by removing larger nonplastics, such as stones. This may be achieved by hand sorting, sieving, winnowing or levigation (Gosselain 2008a:34). The removal of nonplastics that are present in raw clay may introduce compositional variation in the finished ceramics.

Another common processing strategy involves the addition of temper. Temper is generally understood to be the nonplastic material added to clay by potters to reduce shrinkage and decrease the likelihood that a vessel will crack during drying and firing (Shepard 1965:24). Inclusions in the clay body that are not intentionally added, those that are naturally present in the clay, are also referred to as nonplastics. Mineral inclusions, whether natural or added as temper, are easily identified and therefore particularly useful for ascertaining provenance (Shepard 1965:25). However, it is important to determine whether the inclusions are natural, in which case they will be present in the raw clay found at the source, or added, in which case they may have been obtained from a distinct source and will not provide provenance information related to the clay.

Tempers and clays may actually have similar mineralogy, in which case only the relative amounts of plastics and nonplastics determine whether a resource will be considered clay or temper (Arnold 1972:99). Tempers consist *mostly* of nonplastic minerals, and clays consist *mostly* of plastic minerals, but each contains a portion of the other. A potter may mix clays, one naturally containing more nonplastics than the other, in order to achieve the desired consistency. In such cases, the clays are essentially being used to temper each other.

A universal processing strategy is the addition of water to clay during homogenization, to make a plastic building material. The soluble salts present in water

may affect the chemical composition of ceramic vessels (Arnold, et al. 1991), although it is unlikely that their effects would be significant enough to obscure the provenance of a vessel.

2.2.3 Firing

Another factor that may affect ceramic variability is firing. A significant amount of research has been dedicated to determining the effect of firing on ceramic composition (Carpenter and Feinman 1999; Cogswell, et al. 1996; Shepard 1965; Tite 1999). The physical and chemical changes that occur during firing have been well documented. Firing involves three stages: dehydration, oxidation and vitrification (Shepard 1965:20). Most drying occurs before a vessel is fired, but pre-heating may be used to remove any water that has remained, dehydrating the clay. Heat also alters the crystal structure of some minerals, causing them to expand or contract. Quartz in particular is prone to changes in volume as it is undergoes the alpha-beta conversion, and may cause a vessel to break during firing (Shepard 1965:23). Oxidation is accompanied by the decomposition of some mineral inclusions in the clay, particularly carbonates (Shepard 1965:22). If sufficiently high temperatures are achieved, vitrification may occur, which involves glass forming from the alumina and silica left over by the decomposition of clay (Shepard 1965:23). However, the temperatures associated with low-temperature firing techniques (such as bonfires) are rarely sufficient to cause vitrification.

Aside from these physical and chemical changes, there is evidence that some elements and minerals are altered during firing, including bromine (Cogswell, et al. 1996) and calcium carbonate (Tite 1999). However, the consensus is that firing does not significantly alter the chemical composition of ceramics. Whether the alteration that *does*

occur is enough to obscure the relationship between raw materials and the finished product is not well-established.

2.2.4 Summary

This review of the ceramic production sequence demonstrates that natural variability, procurement variables and paste preparation variables all impact ceramic composition. However, they do so unequally. Because ceramic manufacture is an additive process, the behaviour of potters may affect the mineral and chemical composition of final products more significantly than the natural variability of raw materials utilized in production alone (Gosselain 1994; Gosselain and Livingstone Smith 2005). This understanding of ceramic production has major implications for the methods of analysis used in provenance research.

Using compositional data to determine provenance, like stylistic methods, requires comparative material with known origins. Ceramics of unknown provenance may be compared either with raw materials or with ceramics whose provenance is already established. A poor understanding of how the composition of raw materials might be altered during ceramic production has led many researchers to choose the more straightforward method, comparing like with like. This method draws on ceramic samples whose provenance is known, either because they belong to a particular stylistic group (although the risks of relying on style alone have already been touched upon) or because they were recovered *in situ*, from a firing pit or kiln, for example (Rice 1987:413). This comparison of ceramic composition will, however, only reveal whether or not the sample of unknown origin has the same provenance as the control sample. It will distinguish between local and non-local ceramics in terms of archaeological context, but will not

provide information about the origin of non-local ceramics. In order to discover their origin, it would be necessary to compare ceramics with raw materials, and possibly to have raw material samples from a broad area. In order to make a comparison between ceramics and raw materials, one must take into account how composition can change as clay is processed and transformed into a finished vessel.

The characterization technique(s) used to determine the composition of clays and ceramics influence the type of data that will be produced, which in turn affects the types of questions that can be answered. Some techniques are more useful than others when the aim of research is to define provenance and to understand the effects of processing.

2.3 Ceramic Characterization

In ceramic analysis, characterization studies involve qualitative and quantitative descriptions of composition and structure. The constituent elements in ceramics are commonly identified by observing the properties of optical wavelengths or X-rays (Pollard and Heron 2008). A useful method of characterizing ceramic vessels involves observing the interior structure of the ceramic body, including the size, shape, and type of inclusions. The goal of using different characterization techniques is to describe these properties in an objective, precise and replicable manner. The use of a small number of common characterization techniques produces reliable data that can be readily compared with the results of other research.

There are a few standard practices when undertaking characterization studies. One is to begin with less technologically sophisticated methods of observation, like optical petrography, before moving on to more complex ones (Bishop, et al. 1982; Rice 1987). This approach allows researchers to develop a broad understanding of the properties of

the material before delving into more detailed compositional data. It is also common to undertake mineralogical characterization before chemical methods are employed, since chemical characterization provides data relating to the levels of particular elements present in the sample, but does not identify in which minerals those elements occur (Bishop, et al. 1982:288). To obtain a complete picture of the composition of a material, characterization studies generally combine mineralogical and chemical methods.

2.3.1 Mineralogical Characterization Techniques

Following a similar rationale, it is desirable to obtain an initial analysis of ceramics using petrographic techniques. Petrographic techniques have been borrowed from the geological sciences, on the premise that pottery is comparable to metamorphosed sedimentary rocks. Petrographic analysis takes advantage of the atomic structure of minerals, which produces unique properties that can be perceived using optical or instrumental techniques (Rice 1987:376). Using thin sections taken from the body of a ceramic vessel, observations can be made regarding particle orientations, surface treatments, firing alterations, and the size, shape and location of voids within the vessel body (Rice 1987:379). Although these characteristics are not directly useful for provenance research, they may provide information about forming techniques and the effects of processing (Pollard and Heron 2008:101).

Minerals that occur within the ceramic body can be identified using a polarizing microscope to observe the unique optical properties such as colour and refractive index, or by employing X-ray techniques available on a scanning electron microscope. Petrography provides a broad overview of the compositional character of a ceramic

vessel, and information gleaned at this stage of analysis should be kept in mind when interpreting more detailed compositional data.

The mineral composition of ceramics and clays can also be ascertained using techniques that identify minerals based on their crystalline structure. The differences in atomic structure that make minerals identifiable using a microscope also allow them to be identified by their particular diffraction patterns. In X-ray diffraction (XRD) analysis, a specimen is bombarded with X-rays that are diffracted by the atomic planes in minerals, producing a characteristic pattern. Powdered samples are typically used in XRD, which allows the bulk mineralogical composition of a specimen to be determined. Mineralogical composition alone will not usually be sufficient for provenance research, which requires the detailed compositional profiles produced by chemical characterization.

2.3.2 Chemical Characterization Techniques

Chemical analyses of ceramic materials are used to measure the total amount of different elements or compounds present in samples, without distinguishing between clay and temper material, or between the different minerals in which the elements occur. Elements are generally categorized according to their relative abundance in the clay. Major elements are those that occur in amounts higher than 2%, and common major elements in clay include silica, alumina, oxygen, calcium, iron and potassium (Rice 1987:390). Minor elements are those that make up between 0.1 and 2% of the clay body, and generally include calcium, iron, potassium, titanium, magnesium, manganese, sodium, chromium and nickel (Rice 1987:390). Any element that occurs in amounts below 0.1% is considered a trace element. Trace elements are particularly useful for provenance research because of fractionation, which causes them to become more

concentrated in finer-sized fractions as minerals are weathered (Bishop, et al. 1982:295). As a result of this process, discernible chemical differences may be observed between clay sources in areas with low geological variation, or where short distances separate sources.

Most of the methods used to analyze the chemical composition of clays are called spectroscopic methods, because they measure the various wavelengths of energy absorbed or reflected by samples (Rice 1987:392). Chemical techniques that are best suited to point analysis (such as particle-induced X-ray emission, or PIXE) are not ideal in provenance research because they do not ensure that the resulting compositional profiles are characteristic of the entire sample. X-ray fluorescence spectroscopy (XRF) can be employed for both point and bulk analysis, and it is a relatively popular technique in provenance research. One of the more widely used techniques in trace element studies and ceramic provenance research is neutron activation analysis, or NAA. This technique uses a nuclear reactor to irradiate a sample, and then measures the decay rate of the isotopes that are formed (Tite 1999). NAA is capable of identifying a wide range of elements in various concentrations, but it is also very expensive. Similar precision can be obtained with inductively coupled plasma mass spectrometry (ICP-MS), at a fraction of the cost (Kennett, et al. 2002; Tite 1999). Already widely used in the physical sciences, ICP-MS is rapidly replacing NAA as the preferred chemical characterization method in provenance research.

2.4 Provenance Research in South Africa

The principal aim of ceramic characterization research in southern Africa has been to distinguish local and nonlocal ceramics for the purpose of understanding trade

and migration in prehistory (Fowler, et al. 2011; Jacobson 2005; Miller 1991). Although some of these studies compare pots with clays obtained from modern potters, the researchers were primarily concerned with reconstructing the distribution of finished products rather than attempting to associate pots with clay sources. This shared aim has been addressed using a variety of methods, and a number of studies have discussed the relative merits of different characterization techniques.

2.4.1 Previous Research

In the 1970s and 1980s, archaeologists began to explore the potential of geochemical techniques for addressing questions about the movement of people and material culture in southern Africa. The purpose of these early studies was to determine the manufacturing location for different sherds by distinguishing non-local and local samples. The first attempt to use characterization techniques to provenance pottery was made by Boulle and Peisach (1977), using NAA to analyze Namibian ceramic samples. In a later study, they compared the pottery produced by sedentary Bantu peoples with that produced by the Khoisan, who are mobile hunter-gatherers. The authors found that the compositional data reflect mobility patterns; the Bantu samples all related to a single location of manufacture, whereas the Khoisan samples suggested a number of different sources, consistent with a more mobile lifestyle (Boulle and Peisach 1979).

A string of ceramic provenance studies followed, many employing PIXE analysis, which was readily available to researchers in the western Cape (Jacobson 2005:11). These studies used chemical data to define compositional groups, some simply to distinguish between ceramics of different origins (Bollong, et al. 1997; Gihwala, et al. 1984; Gihwala, et al. 1985; Peisach 1986; Peisach, Boulle, et al. 1982a), others to identify

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evidence for the movement of people and pottery (Boulle, et al. 1979; Jacobson, et al. 1991; Jacobson, Pineda, et al. 1994; Peisach, et al. 1990). A diverse range of ceramics were represented in these studies, including samples from Namibia, the former Transvaal (now Mpumalanga) and Northern Cape provinces of South Africa, as well as Chinese porcelain imported during the 18th and 19th centuries.

These early studies had very little previous research to build on, and a significant amount of attention was also paid to methodology and interpretation. As researchers developed a better understanding of the uses and problems with compositional data, a shift in standard methodology occurred. Jacobson (1985) suggested particular sampling and handling protocols for ceramics intended for chemical analysis in order to prevent contamination. Methodology and statistical analyses remained a topic of debate and discussion (Jacobson, Van Der Westhuizen, et al. 1994; Jacobson, et al. 1995; Pillay 2001; Punyadeera, et al. 1999). It was realized that the most effective way to characterize ceramics is to establish the bulk composition of the body, and PIXE is more suited to point analysis. Recognizing this limitation, researchers began to employ XRF as a means of obtaining compositional data. Other researchers compared different multivariate statistical methods, hoping to refine their interpretive capabilities (Bollong, et al. 1997; Peisach, Jacobson, et al. 1982b).

As a result of these developments, studies of ceramics from various regions of South Africa elicited evidence of trade and population movements (Jacobson, et al. 2002; Pillay, et al. 2000; Punyadeera, et al. 1997). These studies built on the interpretive framework of earlier provenance research, developing a more sophisticated understanding of exchange and mobility in prehistory. Taking full advantage of these

advances, Wilmsen and colleagues (2009) combined stylistic and compositional evidence to demonstrate that not only were vessels transported within Botswana, raw clays were also transported from their sources to manufacturing locations great distances away. This study provides an example of how, with careful research design and analysis, compositional data can provide evidence not only for the exchange and transportation of vessels, but also for the decisions and actions of potters.

2.4.2 Critique of Previous Research

Although provenance research in southern Africa has made great strides, problems remain. Previous research has primarily been concerned with distinguishing local and non-local pottery. Such questions have generally been accomplished by comparing pottery whose source is not known with samples whose source is known (often based on style) (e.g. Jacobson, et al. 1991). This approach limits the types of questions that can be studied using compositional data. Using sherds as a comparative material does allow archaeologists to identify non-local ceramics, but it does not make it possible to establish the provenance of any non-local samples. To do so, it would be necessary to directly compare sherds with raw clays. A significant problem with previous provenance studies in southern Africa has been a failure to establish a systematic methodology for comparing the composition of ceramics with raw clays.

Since it has not been established precisely how processing behaviour alters clay composition, researchers often avoid comparing pottery with raw clays, skirting the problem altogether. To successfully relate pottery to clay sources it is necessary to understand the variation present in local clays, and to determine how processing affects composition. Without documenting the variation in composition for local clay sources, it

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is problematic to interpret any variation as a sign of trade or mobility. Furthermore, different processing techniques – used alone or in combination – may cause ceramic vessels to deviate from the composition of their sources to some extent. It is necessary to understand whether that deviation is so great that finished pots cannot be associated with raw clays, or whether the compositional signature of the clay source is still identifiable.

Research has been conducted in Latin America to demonstrate how behaviour affects clay composition, particularly how the use of clays from different sources (and the addition of temper) alters the mineralogy and chemistry of finished vessels (Arnold, et al. 1991; Rice 1978). The results of that research have shown that clay and temper acquisition strategies have a perceptible effect on vessel composition, leading Arnold (1991:87) to conclude that "pottery encodes both chemical information…and behavioural information". However, applications to archaeological cases are few and the links are speculative.

2.5 Research Question

This review of the theory and methods of ceramic provenance research highlights the approaches that may be taken to characterize clays and vessels, and how the resultant data may be used to describe trade and migration in prehistory. More recently, researchers have begun to question their assumption that natural variation is the primary determinant of ceramic composition, and it is generally accepted that processing strategies have the potential to introduce another source of variation. What is not known is whether those different strategies alter composition in a specific and consistent way, making their effects predictable and therefore allowing researchers to compensate for their effects. To assess whether this is the case, it is necessary to determine the

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composition of clay at each stage of processing in order to understand what compositional changes are associated with each step.

In this thesis I investigate the compositional changes that occur when raw clay is transformed into a finished vessel. Through this research, I hope to contribute toward a more thorough understanding of how procurement and preparation variables affect compositional variation in ceramics. I attempt to demonstrate whether it is possible to associate finished vessels with clay sources despite the effects of human behaviour. If so, it will be possible for future provenance research in southern Africa to compare ceramic artefacts with raw clays. This change in methodology would allow archaeologists to move beyond simply identifying local versus non-local pottery, to develop a more accurate reconstruction of ceramic provenance and ceramic production behaviours.

Two hypotheses have been formulated concerning compositional changes in clays during ceramic production:

1) There are observable differences between the mineral and chemical composition of raw clays and finished vessels;

2) These differences can be attributed to cultural factors (i.e. processing) as opposed to geochemical ones (e.g. weathering, depositional factors, and different source compositions).

The null hypothesis is that there is no discernible difference in composition between raw clays and finished vessels. This would indicate that the only significant factor contributing to compositional variability is the source of the raw material.

To test these hypotheses, I have developed a two-step method. First, the mineralogical and chemical compositions of clay are examined at each stage in an

ethnographically documented ceramic production sequence. These analyses were conducted using established mineralogical and chemical characterization techniques (see Chapter 3). Second, I used statistical and qualitative methods to interpret the results, to demonstrate whether the composition of a finished vessel is different from that of the raw clay from which it is made. In addition, I compared the composition of clay at each point in the production sequence to identify whether composition changed as a result of particular processing methods.

In sum, this thesis is a response to a disconnect between theory development and advances in analytical methods in archaeological provenance research. The technical instrumentation of materials analysis has advanced rapidly, faster than the theory that is required to understand how cultural behaviour can be interpreted from characterization data (Rice 1987:328). Systematic study of the relationship between procurement and preparation variables of ceramic production and the composition of finished vessels is one step toward an adequate interpretive framework.

Chapter 3. Materials and Methods

3.1 Study Area

The collection used in this thesis derives from a study area in the Lower Thukela Basin, in the province of KwaZulu-Natal, South Africa. The Lower Thukela Basin extends approximately 4500 km^2, and contains a number of eco-zones ranging from mountains and plateaus to valleys and coastline (Figure 3.1). The study area is located in the central portion of the basin, and falls mainly within the municipality of Nkandla. Since the borders of the municipality generally follow the outline of the central basin, I will refer to the study area as Nkandla. Ceramic production in this region has been well documented over the last two decades (Armstrong 1998; Armstrong and Calder 1996; Armstrong, et al. 2008; Fowler 2006, 2008; Jolles 2005; Reusch 1998). The geology of the region has also been the subject of detailed study (Matthews and Charlesworth 1981; van der Eyk, et al. 1969; Whitmore, et al. 2006). This extensive documentation makes Nkandla an ideal location for the detailed study of ceramic production and provenance.

3.1.1 Geology of the Lower Thukela Basin

The Nkandla study area centres on the confluence of the Nsuze and Thukela rivers. The rolling plains and hills of the Lower Basin are covered by low bush and grasslands. A number of seasonally-inundated streambeds run down from the hills towards the two rivers, and the exposed stratigraphy of dry streambeds provides an ideal opportunity for identifying and accessing clays.
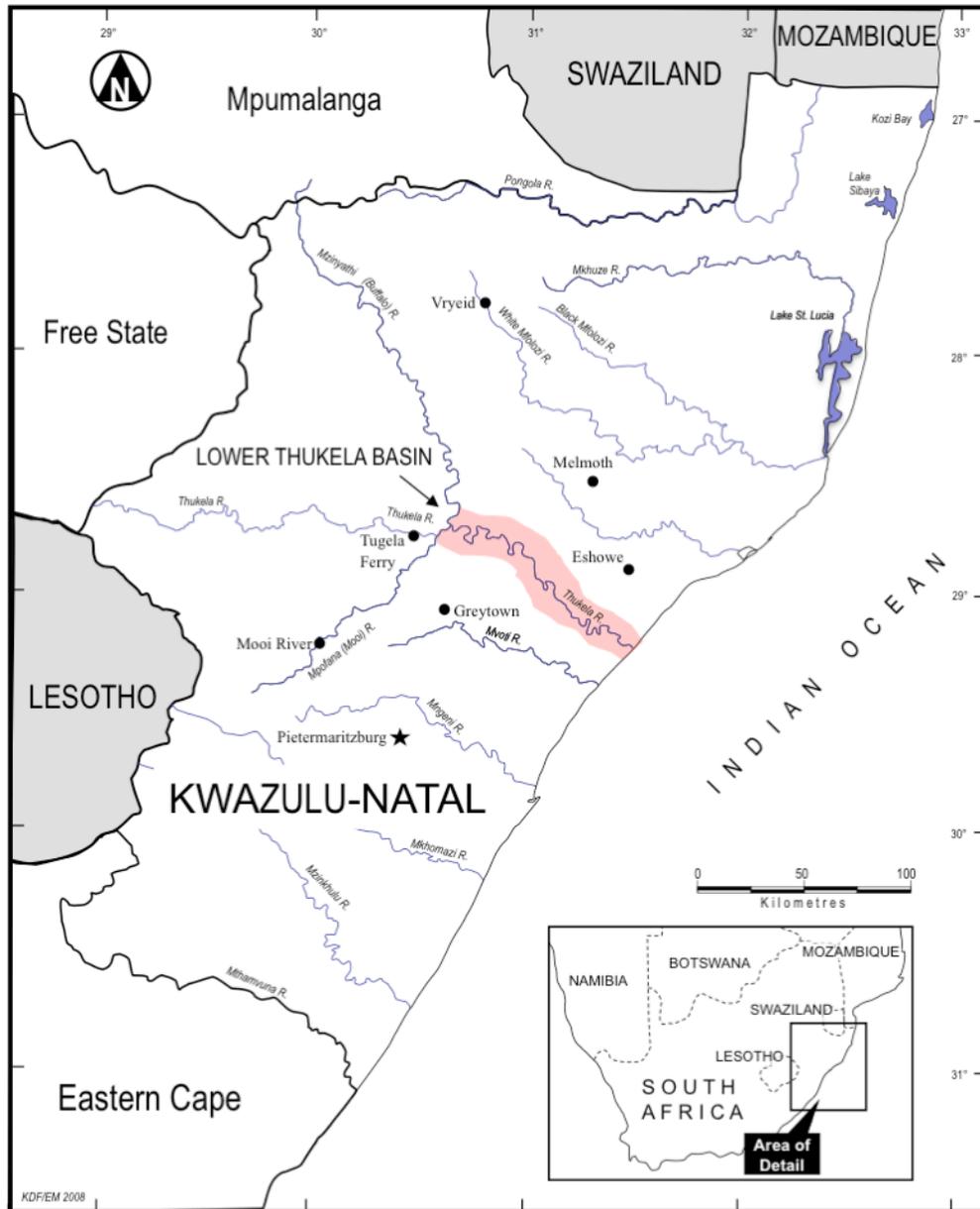
Figure 3.1 Map of KwaZulu-Natal showing the Lower Thukela Basin. (From Fowler 2008: Figure 1, used with permission.)

The foundation of KwaZulu-Natal geology is made up of two separate continental blocks that collided approximately 1000 million years ago. The northern block, the Kaapvaal Craton, is the oldest crustal block in southern Africa, formed 3000 million years ago when granite intruded into the basaltic crust of the Earth (Whitmore, et al. 2006). The Craton is composed primarily of granite, and contains greenstone fragments. Within the Craton, Nsuze Group basalts alternate with marine and fluvial sandstones. The Natal Metamorphic Province was created in the southern block, as the Namaqua-Natal Mobile Belt collided with the Craton. Rocks in this section were heated and deformed into a mountain range, which was subsequently eroded to expose the granite and gneiss below (Whitmore, et al. 2006).

The first deposits on the newly formed Metamorphic Province constitute the Natal Group sandstones that were deposited by rivers nearly 500 million years ago (Whitmore, et al. 2006). During a subsequent glacial period, a thick layer of Dwyka Group tillite was deposited by retreating ice sheets. Extending from the Transvaal into KwaZulu-Natal are Ecca Group shales and sandstones, formed from the bed and shorelines of a large sea (Whitmore, et al. 2006).

The folding caused by the collision of these continental blocks formed a number of nappes, which characterize the surficial geology of the central basin (Figure 3.2). The Madidima Nappe makes up a large portion of the central basin, composed of the mica gneisses and schists of the Gazeni Formation, and amphibolites of the Zwaneni Formation (Matthews and Charlesworth 1981). At the periphery of the central basin are Dondwana (grey biotite-feldspar and hornblende-biotite gneiss) and Wosi (amphibolites and magnetic quartzite) Formations of the Mandleni Nappe, as well as Halambu

Figure 3.2 Geological map of Nkandla showing clay sources. Clay source numbers refer to data in Table 3.2.

Granitoid Gneiss from the Nkomo Nappe (Matthews and Charlesworth 1981). The Thukela River also passes through the Manyane and Tuma Formations, which are characterized by amphibolites, felsic gneiss and tremolite-chlorite schist (Matthews and Charlesworth 1981).

Deep, red soils have been formed in the central basin by amphibolites and quartzitic alluvium (Maphumulo 1986; van der Eyk, et al. 1969). These alluvial sediments have produced kaolin-rich secondary clays (Fowler 2008:485). Previous analysis of clay and vessels from this area suggest they are composed of minerals consistent with the local geology, primarily quartz, feldspars, metamorphic limestones and granites, as well as calcite and micas (Fowler 2002).

3.1.2 Ceramic Production in the Lower Thukela Basin

Documentation is available for two groups of potters that reside in Nkandla. The potters practice their craft in two homesteads, referred to by the names *Salakahle Magwaza* and *Zibuse Magwaza*. The techniques used to process raw clay have been described for each group, providing a known sequence of steps. Ceramic production in Africa is generally considered to be a female activity (Gosselain 2008a), and this is true in Zulu society as well. Zulu pottery production can be divided into seven stages of manufacturing, consistent with Gosselain's (2008a) overview of African pottery production (also see Fowler 2006, 2008, 2011, in press). Those stages include resource procurement, processing, vessel shaping, decoration, drying, firing, and post-firing treatment (Gosselain 2008a:32). Not every stage in the production sequence will affect the composition of a ceramic vessel. Although I will describe each step here, my analysis will only be concerned with those stages that may alter composition.

3.1.2.1 Resource Procurement

Potters in Africa – as in most parts of the world – typically obtain clay from sources within three kilometres of their home or manufacturing location (Arnold 1985; Gosselain 2008a). Clay may be collected wet or dry, using a variety of extraction techniques. If clay is exposed on the ground or in an eroded bank, it may be collected from the surface. For clay that is further underground, pit extraction may be required. Clay may also be collected from streambeds or riverbeds. Temper may be collected using similar methods. Temper may be mined, in the case of rocks and minerals, or collected from the surface, in the case of ash, shells, or organic material. No extraction techniques are required if a potter chooses to use grog (ground-up potsherds) as a tempering material, since broken pieces of pottery are readily available.

Potters in Nkandla employ a compounding resource procurement strategy. They exploit six clay sources in the vicinity and mix clays from the different sources. These sources can be up to seven kilometres away from the potters' homesteads, but those most heavily exploited are within three kilometres (Fowler 2008:487). Three sources are characterized as red clay, and three as black clay. Dry clay is collected from exposed strata in streambeds, where it is chipped out with a heavy tool such as an axe or hoe blade (Fowler 2008:487). Hard lumps of clay must be processed to produce a finer material for vessel forming.

3.1.2.2 Clay Processing

There are four categories of processing techniques that a potter can choose to employ: pre-treatment, the removal of nonplastics, the addition of nonplastics, and homogenization (Gosselain 2008a). Pre-treatment of clay may include drying, grinding, soaking, or souring, each of which helps produce a clay body with the desired consistency and malleability. The removal of nonplastics is typically conducted by hand (picking out individual pieces of rock), using a sieve, or by winnowing. More complex strategies, such as levigation, are rarely used by African potters (Gosselain 2008a:34). Nonplastics may be added to clay as temper, or clays may be mixed together to produce a clay body with desired characteristics. During homogenization water is added to the clay, which is kneaded or pounded until it reaches the preferred consistency and is ready to use.

In Nkandla, processing of raw clays involves 1) pre-treatment (drying the clay), 2) pounding and grinding, as well as sieving and hand-sorting to remove nonplastics, 3) tempering (mixing clays), and 4) homogenizing the paste (adding water and kneading). Although the hard clay collected from exposed streambeds is fairly dry, it may be laid out in the sun to remove any remaining moisture before grinding takes place. When the clay is completely dry, potters use a rounded river cobble and a flat grinding stone (or simply a sack placed on a cement floor) to grind clay into a fine powder (Fowler 2008:489). Visible rocks may be removed by hand, but the clay powder will also be passed through a sieve to remove any large nonplastics (Fowler 2008:489). When making very large vessels, called *izimbiza*, that are used for fermenting beer, clay is not sieved because the

nonplastics in the clay have a tempering effect which strengthens the vessel (Armstrong, et al. 2008:521).

Potters in Nkandla use a combination of red and black clay to manufacture vessels, in order to achieve the ideal level of plasticity and shrinkage (Fowler 2008:490). The ratio of red to black clay varies depending on the size and function of the desired vessel, but it is generally about half and half (Fowler 2008:490). After the clay has been processed water is added, and the clay is kneaded to create a malleable material.

3.1.2.3 Shaping and Decoration

In many communities throughout Africa the shaping process involves an initial phase of "roughing out", during which the walls of a vessel are constructed with little concern for their form (Gosselain 2008a). This rough stage is followed by "pre-forming," when the walls are manipulated to take on the desired shape of the finished vessel (Gosselain 2008a). Once the vessel begins to take on its final shape, the walls are smoothed. Decoration may follow this stage, or the pot may be left plain.

Regardless of the size or intended use of the pot, all vessels are constructed using a coiling technique. A flat disc of clay is formed for the base of the pot, and coils are added around the circumference to build the walls of the vessel (Fowler 2008:491). The walls are then scraped with a flat tool, to join the coils and smooth the surface. When the vessel is partially dry, it may be decorated. Designs may be cut or stamped on the surface of the vessel, or appliqué techniques (attaching clay shapes to the surface of a vessel) may be employed (Fowler 2008:491). When decoration is complete, vessels will be left to finish drying before they are fired.

3.1.2.4 Drying and Firing

Vessels need to be air-dried before they can be fired, to remove most of the water from the clay and to prevent cracking. Depending on the season and the weather, this may take anywhere from a few days to a number of weeks. In the summer, drying time is shorter than in the winter, but vessels are always kept in the shade to prevent them from drying too quickly. When it comes time to fire vessels, a number of factors are involved. The schedule and location of the firing need to be determined, fuel must be collected, and the positioning of the vessels and fuel within the firing area must be considered (Gosselain 2008a).

The types of fuel used to fire ceramics in Africa can be characterised as "light" and "heavy" fuel (Gosselain 2008a:39). Light fuel includes grass or straw, manure, leaves, bark, and twigs. Heavy fuel includes denser material, such as branches and logs. These fuels may be used in combination or along.

Potters in Africa utilize a variety of firing structures. The most common and widespread of these is the open bonfire, which involves fairly low temperatures and a simple structure. Elaborations on this structure may include forming a depression or pit to hold the vessels, elevating the fire off the ground, or even the construction of a shield to isolate vessels from direct contact with the fuel (Gosselain 2008a). More complex firing structures include ovens and updraft kilns, but these are relatively rare in sub-Saharan Africa (Gosselain 2008a).

During the dry winter months in Nkandla, an open bonfire is built on a level area of ground (Fowler 2008:497). In the summer, when rain is more common, a layer of ash is spread in a shallow depression to shield the fire from moisture (Fowler 2008:497). The

potters use grass, wood, dried aloe leaves, and *Euphorbia tirucalli* branches as fuel (Armstrong, et al. 2008; Fowler, et al. 2011). Vessels are placed on a layer of fuel and covered with dried leaves and branches (Armstrong, et al. 2008; Fowler 2008). This method of firing involves fairly low temperatures, reaching maximum internal temperatures just over 900˚C (Armstrong, et al. 2008:522). Firing is generally complete in less than an hour, after which vessels are removed from the fire to cool, and then stored for subsequent post-firing treatments.

3.1.2.5 Post-firing Treatment

It is common in sub-Saharan Africa for vessels to receive a final treatment after firing. This treatment may occur directly after firing, such as when water is sprinkled on hot vessels, or it may take place once vessels have cooled (Gosselain 2008a:41). Cooled vessels may be coated in manure or resin, smoked and coated in soot, or smeared with oil or fat. In some cases these treatments are used to achieve a particular appearance, and in others they are believed to ensure certain properties, such as water-tightness.

Post-firing treatment in the study area involves a second, low-temperature, firing. This firing is used to blacken drinking and serving vessels, carbonizing the exterior of the pots with soot (Armstrong, et al. 2008:524). The fuel for this second firing may include grass, wood, dung, and old rubber shoe soles (Fowler 2008:497). This second firing is appropriately characterized as a bonfire with separation, because the pot is placed on a tripod above the fire. After the second firing, pots are coated in shoe polish to create a glossy sheen (Fowler 2008:497). Large brewing vessels (*izimbiza*) are not blackened. Instead, a dried maize cob is used to roughen the exterior of these vessels, and a mixture of dung and water is applied to the surface (Armstrong, et al. 2008:526).

Table 3.1 List of analytical samples.

Analytical Sample #	NCSP Sample #	Sample Type	Processing Stage	Clay Source
1	22a	clay	unprocessed	Siqumama
2	22b	clay	ground & sifted	Siqumama
3	23b	clay	ground, sifted & mixed	Siqumama, Nokhona
4	23d	clay	mixed nonplastics	Siqumama, Nokhona
5	24a	clay	mixed nonplastics	Siqumama, Nokhona
6	25	clay	ground, sifted & mixed	Siqumama, Nokhona
7	26a	clay	unprocessed	Nokhona
8	26b	clay	nonplastics	Nokhona
9	26c	clay	ground & sifted	Nokhona
10	28a	clay	unprocessed	Ntontonto
11	28c	clay	ground & sifted	Ntontonto
12	28e	clay	nonplastics	Ntontonto
13	37b	vessel	fired	Siqumama, Nokhona
14	40b	vessel	fired	Siqumama, Nokhona
15	44b	vessel	fired	Siqumama, Nokhona
16	45b	vessel	fired	Siqumama, Nokhona
17	48b	vessel	fired	Siqumama, Nokhona
18	50b	vessel	fired	Siqumama, Nokhona
19	51b	vessel	fired	Siqumama, Nokhona
20	57	clay	ground & sifted	Ntontonto
21	58a	clay	unprocessed	Ndondondwane
22	58b	clay	ground & sifted	Ndondondwane
23	58c	clay	nonplastics	Ndondondwane
24	59a	river clay	unprocessed	Nsuze River
25	353b	vessel	fired	Ndondondwane, Nokhona
26	MAG4B	clay	ground	Ndondondwane
27	22c	clay	nonplastics	Siqumama

3.1.3 Materials

The samples used for this study were collected as part of the Nguni Ceramics and Society Project (NCSP), under the direction of Dr. Kent Fowler at the University of Manitoba. The NCSP collection includes materials from four study areas in southern Africa (Fowler 2008, 2011, in press); for the purposes of this research I chose to focus on a single region, the Lower Thukela Basin. Restricting this analysis to one region will allow me to investigate subtle changes in clay composition, rather than the broad compositional differences that would dominate a multi-regional analysis. It will also permit me to assess the geographic scale at which provenance may be determined based on the composition of sources.

3.1.4 Analytical Samples

Twenty-seven samples were selected for analysis, including eight finished vessels, five raw clays, and fourteen processed clay and nonplastic (fragments of rocks or minerals) samples (Table 3.1). Samples are included from each stage in the processing sequence, including raw clay, ground clay, sifted clay, the nonplastics removed during sieving, as well as mixed clays. The raw clay samples represent four clay sources used by potters and one sample of local river clay that is used as a building material, which has been included to assess compositional variety in the area.

Potters use a mixture of red- and black-coloured clay to produce vessels. Red clays contain higher levels of iron oxides, as well as coarser rock and mineral components (Fowler 2008:485). Black clays have high organic content, and contain small, rounded minerals (Fowler 2008:486). Potters exploit two black clay sources in the

area, referred to as *Siqumama* and *Ndondondwane* (see Table 3.2 and Figure 3.2). *Siqumama* is located less than two kilometres away from both homesteads, and both groups of potters collect clay from this source (Fowler 2008:486). *Ndondondwane* is located south of the Nsuze River, approximately 2.5 kilometres away from the *Salakahle Magwaza* homestead, and it is occasionally used by potters from that homestead (Fowler 2008:486). Red-coloured clay is available at two sources north of the Nsuze River, *Nokhona* and *Ntontonto* (Table 3.2 and Figure 3.2). *Nokhona* is the closer of the two, located within two kilometres of the homesteads, and it is use by both groups of potters. *Ntontonto* is the most distant source, approximately seven kilometres away, and it is only used by *Salakahle Magwaza* potters (Fowler 2008:486). However, the distance is prohibitive, and this source has mostly fallen out of use.

Table 3.2 Clay sources used by potters in Nkandla. Data from Table 1, in Fowler (2008:497).

Clay Source	Clay Type	Source Name	Utilized By	Geodesic Distance (km)
1	Black	Siqumama	Salakahle Magwaza	1.80
			Zibuse Magwaza	1.40
2	Red	Nokhona	Salakahle Magwaza	1.90
			Zibuse Magwaza	1.00
3	Red	Ntontonto	Salakahle Magwaza	6.70
4	Black	Ndondondwane	Salakahle Magwaza	2.50

Clay samples for some stages of processing were collected in the field, and where they were unavailable, samples were manufactured in the lab. Samples from each clay source were collected in the field (analytical Samples 1, 7, 10 and 21). Nonplastics from a

mixture of red and black clays from were obtained from both homesteads (Samples 4 and 5). The sieved, mixed clay from which those nonplastics were removed was obtained at the *Zibuse Magwaza* homestead (Sample 6). A sample of sieved red clay (Sample 20) was collected from *Salakahle Magwaza*. Also included in the analyses was a sample of ground black clay (Sample 26) and a sample of coarse clay used in the construction of houses (Sample 24), both collected by Fowler during fieldwork in 2002.

Using raw clay from each of the four sources, samples representing each processing stage were prepared in the lab. Raw black clay from *Siqumama* was ground using an agate mortar and pestle, and sifted using a 1 mm geological sieve, producing samples of sifted black clay and nonplastics (Samples 2 and 27, respectively). The same was done with red clay from *Nokhona* to produce sifted red clay and nonplastics (Samples 9 and 8, respectively). Red clay from *Ntontonto* was ground and sieved to obtain a sample of nonplastics (Sample 12) that corresponds with sifted red clay collected in the field (Sample 20, listed above). Black clay from *Ndondondwane* was also ground and sieved to produce sifted black clay and nonplastics (Samples 22 and 23, respectively).

Eight finished vessels from the NCSP collection were selected to be included in analysis, four from the *Salakahle Magwaza* homestead (Samples 13-16) and three from the *Zibuse Magwaza* homestead (Samples 17-19). The latter was limited to three vessels because part of the collection was still in transit from South Africa. The last vessel included in the analysis (Sample 25) was also obtained from the *Salakahle* homestead, but it was purchased in 2002, before sieves were used to remove nonplastics during the processing sequence. Comparing the composition of this pot with more recent ones will

help determine the different effects of sieving and hand-sorting on mineral and chemical composition.

3.2 Methods

A combination of mineralogical and chemical characterization methods was used to obtain bulk and point compositional data. Petrographic data was obtained using a scanning electron microscope (SEM). X-ray diffraction (XRD) was used to analyze bulk mineralogy for each sample. The bulk chemical composition of samples was analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

In all cases, samples were removed from whole vessels using a diamond bit on a Dremel 400 XPR saw, as well as a hacksaw. To prevent contamination by the blackened exterior of the vessels (e.g. soot, industrial resins), the surface of each sample was removed using a steel burr on the Dremel saw. The saw bit and burr were cleaned with ethanol and distilled water before preparing a new sample.

3.2.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is capable of detecting different types of beams that result from the collision of electrons with atoms in a sample. These beams each relay different information about a sample. Electrons that are reflected from the sample are called back-scattered electrons (BSEs). An image of the sample can be obtained using BSEs that carries some basic chemical information; bright areas on the image have a higher atomic number than dark areas (Vladar and Postek 2009:460). More detailed elemental information can be obtained using energy dispersive X-ray spectroscopy (EDS). As electrons hit the sample, they may liberate electrons from the

inner shells of atoms within the sample, creating gaps that are filled by electrons from outer shells. During this transfer, excess energy is emitted as an X-ray, and the energy of this X-ray is characteristic of the element from which it originates (Roomans and Dragomir 2007:507). Mineral inclusions in a ceramic body can be identified using these X-ray emissions, but not the clay matrix itself, which requires bulk analysis.

Polished thin sections of vessels were prepared for SEM analysis. A small piece of ceramic material ($<1cm^3$) was embedded in resin, which was placed under vacuum to remove air pockets and draw the resin into the ceramic body. Using a Buehler Isomet 1000 Precision Saw, the resin puck was halved through the middle of the ceramic sample. The exposed surface was then polished using successively finer-grit sand paper (400, 800, 2000 and 4000), and was adhered to a glass slide with additional resin. After the resin was completely hardened, a Buehler Petro-thin Thin Sectioning System was used to cut and grind the remaining resin to a thickness of approximately 70 microns. The sample was then polished by hand using the same sequence of sand paper grit until it reached a thickness of 30 microns.

Thin sections were adhered to the SEM mount using carbon tape, which helps diffuse charge build-up caused by electron bombardment, and the slides were carbon-coated. Samples were analyzed with a Cambridge Stereoscan 120 scanning electron microscope, and with a BSE detector and an EDS detector with digital imaging. BSE images were captured and individual mineral grains were identified using EDS at magnifications of 20x, 50x, and 100x. However, at high levels of magnification it became difficult to obtain an accurate identification, as the beam began to pick up readings from the paste surrounding individual grains. Also, the carbon coating on some thin sections

was not evenly distributed, causing the sample to become charged in the instrument and compromising the image quality. Better results were obtained by removing the carbon coating and applying a gold coat to the samples. The spectra for gold-coated samples displayed a peak for gold, which was dismissed during analysis.

3.2.2 X-Ray Diffraction (XRD)

Bulk mineralogical composition can be ascertained using X-ray diffraction (XRD), which identifies minerals based on their crystalline structure. This technique takes advantage of the fact that the atomic planes of different minerals diffract X-rays to varying degrees. Bombarding a sample with X-rays produces a diffraction pattern that is characteristic of the minerals in the sample. The diffraction pattern creates a profile that can be analyzed using software to compare it with known mineral profiles.

Samples for XRD analysis must be ground into a fine powder and adhered to a glass slide. All samples (vessels, clays, nonplastics) were ground in an agate mortar and pestle to form a fine powder. A small portion (approximately one gram) of powdered sample was subsequently ground further in a smaller mortar with a few drops of ethanol, creating a slurry, which was then allowed to dry. The resultant powder was placed on a glass slide and spread in a square of even thickness in the centre of the slide. Drops of ethanol were placed around the edges of the sample, which was smeared using a fine-tipped tool, allowing the grains to settle in a very thin layer on the slide. After the ethanol had evaporated, the sample remained adhered to the slide and was ready for analysis.

Prepared samples were analyzed using a Siemens D5000 powder diffractometer, with a rotating anode emitting CuKα radiation and MDI Data Scan software. Samples were scanned with a theta range of 3 to 70, at increments of 0.02 with a scan speed of 2

seconds. The resulting spectra were analyzed using MDI Jade 7.5 XRD software to determine what minerals were represented in the sample.

3.2.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is widely employed in the physical sciences. This technique is destructive, but the size of the sample analyzed can be fairly small (about five grams). In ICP-MS, aerosolized samples are passed through a torch, which ionizes the constituent elements. These elements are then fired towards a quadrupole detector, where ions are separated according to their mass by alternating the voltage on two sets of oppositely charged rods (Kennett, et al. 2002:444). Ions of a particular mass are able to pass through the quadrupole into the detector cups of the mass spectrometer. The voltage in the quadrupole can be alternated during analysis, scanning the full range of elements (Kennett, et al. 2002:445).

Samples were prepared in the same manner as the XRD samples, inclusive of the first round of powdering in the agate mortar and pestle. These samples were then shipped to ActLabs in Ancaster, Ontario for final preparation and analysis.

At the ActLabs facilities, samples are crushed to approximately 100 microns and fused in preparation for analysis. The sample is mixed with lithium metaborate and tetraborate in a graphite crucible, and introduced into a furnace at 1150 degrees Celsius (ActLabs n.d.). After being placed in a mixture of 5% nitric acid, the mixture is dissolved, and ready for ICP-MS analysis. The fusion method employed by ActLabs for their lithogeochemistry services measures major oxides and trace elements, including rare earth elements (ActLabs n.d.). For analysis, the fused sample is diluted and analyzed using a Perkin Elmer Sciex 6000, 6100 or 9000 ICP-MS (ActLabs n.d.). Controls are

analyzed before and after the sample group, and duplicate samples are analyzed at regular intervals within the sample group (ActLabs n.d.).

3.3 Summary

Potters in the Lower Thukela Basin follow a documented production sequence when manufacturing ceramic vessels. A number of steps within that production sequence have the potential to alter the composition of clay, particularly the processing stage when material is added to or removed from raw clay. Samples were obtained and analyzed for each stage in the production sequence. A combination of mineralogical and chemical techniques was used to characterize clay and ceramic samples. SEM was used to examine the general character of vessels (e.g. the size and distribution of inclusions), and to obtain mineral identifications of inclusions. The bulk mineralogy of each sample was analyzed using XRD. Detailed measurements of the concentration of major and trace elements were obtained using ICP-MS. Comparisons of the mineralogical and chemical data amongst clay sources, processed clays, and finished vessels are presented in Chapter 4.

Chapter 4. Results

The mineralogical and chemical analyses undertaken for this study produced qualitative data related to the mineralogical composition of clays and vessels, as well as the observable structural characteristics of vessels in thin section. Combined with the quantitative compositional data produced by chemical analysis, these will be used to assess the effects of processing behaviour on provenance determination.

Statistical analyses were used to provide a general overview of the chemical data, how they are related to clay sources and the strength of those relationships. The chemical data take the form of concentrations for each element, in percentages for major elements, and in parts per million (ppm) for trace elements (see Appendix A). The concentrations of four trace elements (As, Ag, In and Bi) are below the detection limits of ICP-MS, and these elements are omitted from analyses.

Analyses were performed using the IBM SPSS® Statistics program version 19. Dot-plots were produced for each element, to reveal unique features and potential groupings within the data. The compositional similarities between particular samples that became apparent in these dot-plots were confirmed in subsequent analyses. Multivariate statistics were used to assess compositional groupings. Both principle component analysis (PCA) and cluster analysis are commonly used in provenance research, either alone or in combination. PCA provides a two-dimensional representation of groups in the data, separating specimens according to the elements that explain the most variation in the data set (Baxter 1994:50). Specimens that group together have similar compositions,

but the two-dimensional plot does not explain the relationships *between* those groups. To examine those relationships, it is necessary to resort to cluster analyses.

Cluster analysis also identifies groups based on their compositional similarity, using specified algorithms to amalgamate clusters. For compositional data, it is most effective to use hierarchical agglomerative methods, choosing algorithms that compare groups as a whole, rather than comparing individual members within those groups (Baxter 1994:146). Two algorithms that meet this requirement are Average Linkage and Ward Linkage. True to its name, Average Linkage compares the average composition of all members of a group, and amalgamates groups that have a similar composition. Ward Linkage merges clusters so that the overall increase of variability within the new cluster will be minimized. Because these algorithms use different rationales for merging clusters they can produce different results, and the results should be compared to look for relevant relationships that can be identified using either method. Cluster analysis requires subjective interpretation to determine which groupings are significant. PCA provides a means of assessing the resulting clusters, and cluster analysis can provide insight into the degree of relatedness between different groups. For this reason, the strength of interpretation is increased when these analyses are used in combination.

Results of the mineralogical and chemical characterization of clays and vessels will be presented in four stages. First, the results of mineralogical analyses will be presented. Second, I will then provide an overview of the compositional groups that appear to be present in the chemical data. Third, the specific chemical composition of each clay source will be discussed, highlighting features that are characteristic to each

source. This will be followed by a description of the chemical composition of processed clays. Lastly, the chemical composition and of fired vessels will be presented.

4.1 Results of Mineralogical Analyses

Mineralogical analyses were conducted prior to chemical characterization, to understand how the presence of particular minerals might be reflected in the chemistry of samples. Vessels were analyzed using SEM to identify individual mineral grains, and to examine the physical character of the clay body. Bulk analysis was then conducted for all samples, using XRD.

The identification of mineral inclusions in SEM analysis provides a fairly detailed picture of the mineralogical composition of finished vessels. Significant amounts of quartz are present in all vessels (Samples 13-19 and 25, Table 4.1). Both plagioclase and alkali feldspars are represented in all samples: albite and orthoclase occur in all samples, and anorthite occurs in Samples 19 and 25. Pyroxenes and amphiboles are also ubiquitous, mainly in the form of augite, hornblende and magnesio-hornblende, although specific identifications are inconclusive. A low-calcium orthopyroxene appears to be present in Sample 13, possibly pigeonite. Sample 16 contains a mineral high in chromium (Cr), possibly chromite. Other minerals that could be identified in many samples include ilmenite, magnetite, muscovite, biotite and titanite. These minerals are very typical of igneous and metamorphic rocks, as well as the amphibolites that are so prevalent in the regional geology.

Back-scattered electron (BSE) images of the vessels allow observations to be made regarding the physical characteristics of different ceramic vessels. Some variation can be observed in the characteristics of vessel samples, particularly in the size of

Table 4.1 Results of SEM analysis.

Analytical Sample #	NCSP Sample #	Sample Type	Source(s)	SEM Results
13	37b	vessel	Siqumama & Nokhona	quartz, albite, orthoclase, plagioclase, amphibole (hornblende?), pyroxene (augite?), orthopyroxene (pigeonite?), ilmenite, possibly muscovite
14	40b	vessel	Siqumama & Nokhona	quartz, albite, orthoclase, plagioclase, amphibole, pyroxene (augite?), titanite, possibly biotite
15	44b	vessel	Siqumama & Nokhona	quartz, albite, orthoclase, plagioclase, amphibole, pyroxene (augite?), ilmenite, muscovite, biotite, magnetite
16	45b	vessel	Siqumama & Nokhona	quartz, albite, orthoclase, plagioclase, amphibole (magnesio-hornblende?), pyroxene (augite?), ilmenite, biotite, possibly chromite
17	48b	vessel	Siqumama & Nokhona	quartz, albite, orthoclase, plagioclase, amphibole, pyroxene (augite?), biotite
18	50b	vessel	Siqumama & Nokhona	quartz, albite, orthoclase, plagioclase, alkali feldspar, amphibole, pyroxene (augite?), ilmenite, possibly biotite
19	51b	vessel	Siqumama & Nokhona	quartz, albite, orthoclase, plagioclase, anorthite, amphibole, pyroxene (augite?), ilmenite, possibly biotite
25	353b	vessel	Ndondondwane & Nokhona	quartz, albite, orthoclase, anorthite, amphibole, pyroxene (augite?), ilmenite, possibly biotite
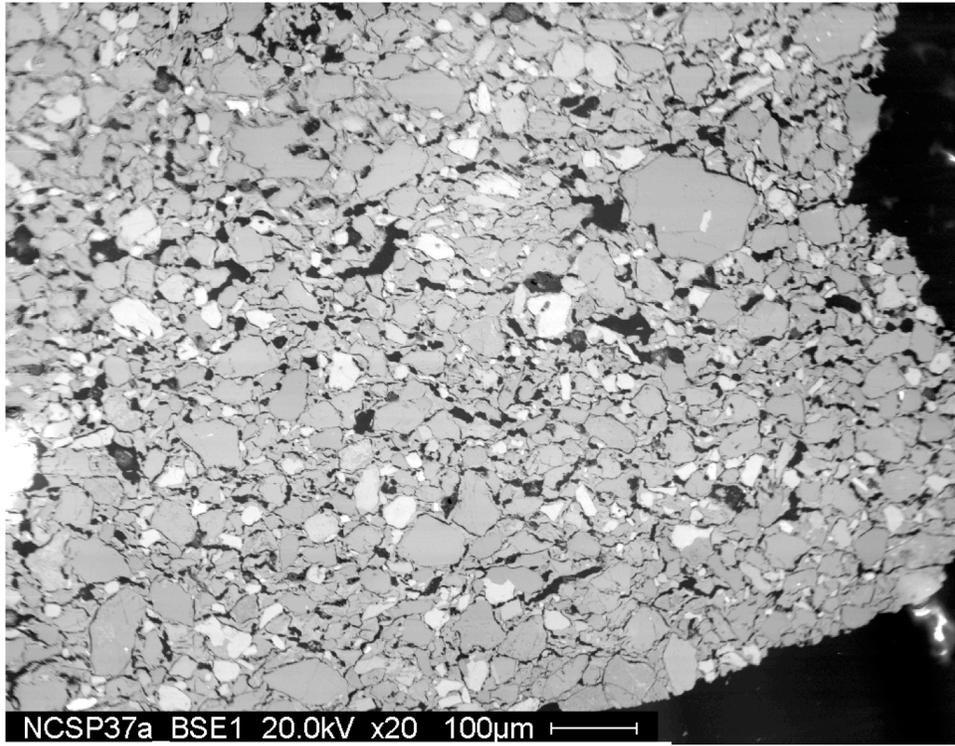
Figure 4.1 BSE-SEM image of vessel Sample 13.
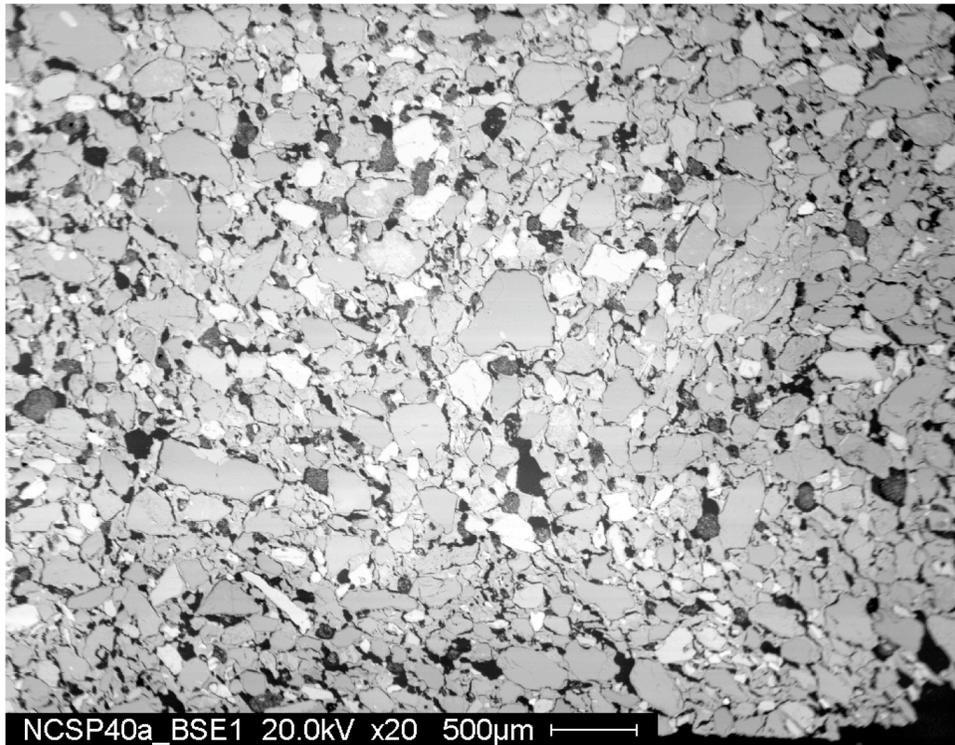
Figure 4.2 BSE-SEM image of vessel Sample 14.
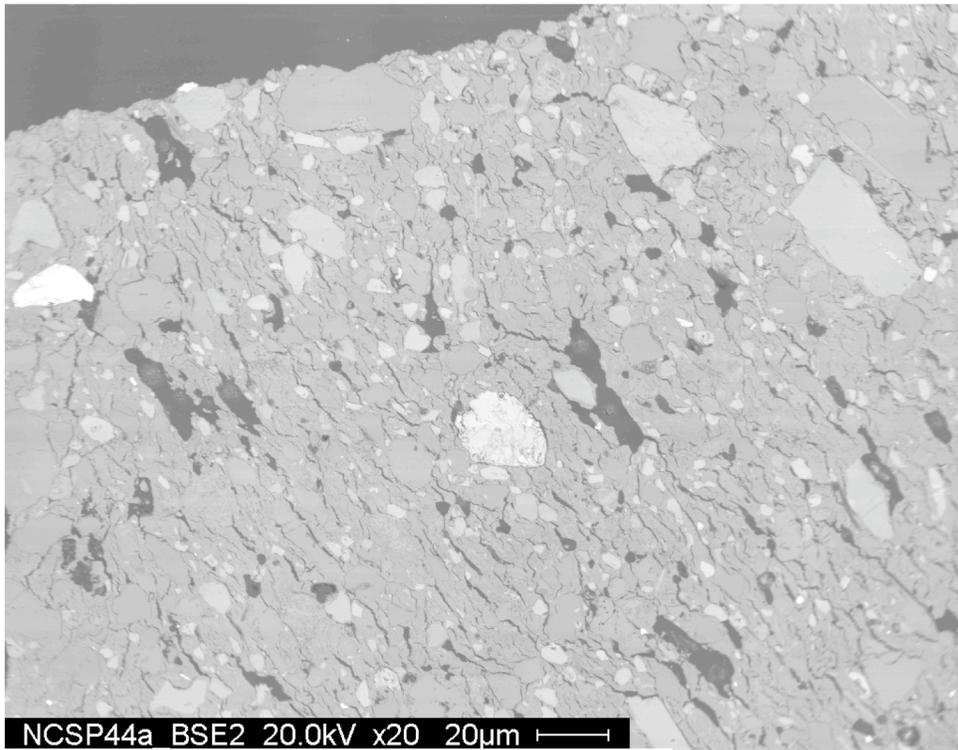
Figure 4.3 BSE-SEM image of vessel Sample 15.
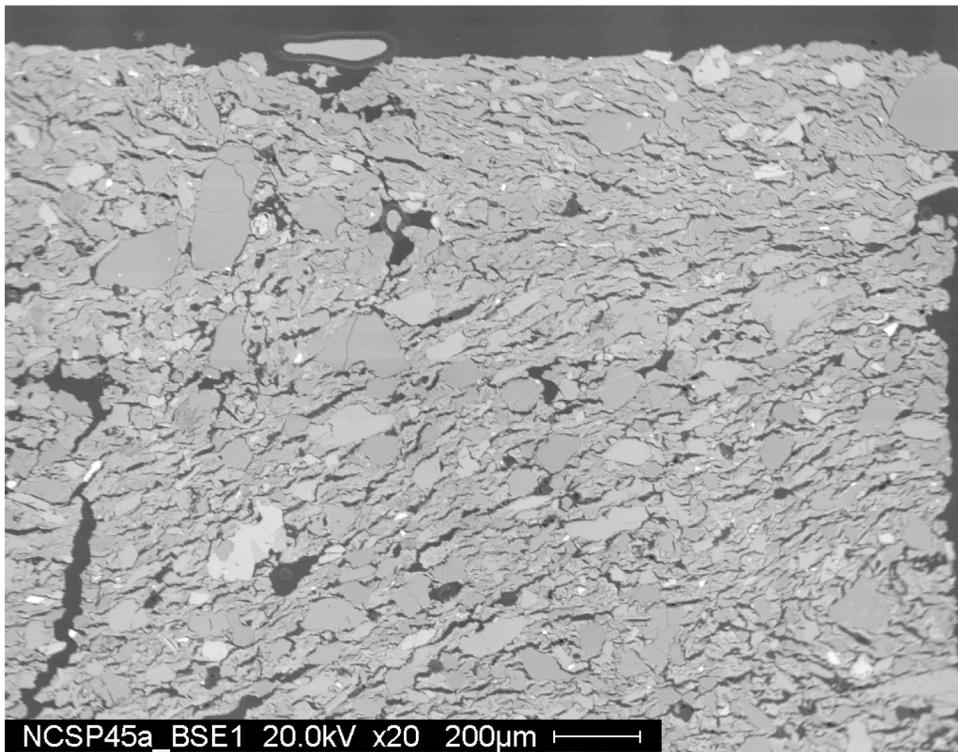
Figure 4.4 BSE-SEM image of vessel Sample 16.

inclusions, as well as the size and shape of voids in the clay structure. The size of inclusions in Sample 13 varies from approximately 25-300 μm (Figure 4.1). The clay matrix itself is not dense, but has a large number of voids between inclusions. Sample 14 has a wide range of inclusion sizes, from 100-600 μm, and contains numerous voids (Figure 4.2).

Sample 15 has a very homogeneous composition, with numerous small inclusions ranging from 5-45 μm (Figure 4.3). The voids in Sample 15 are mainly very thin, and oriented in a laminar pattern. The few large voids that are present are all elongated in the same direction. Sample 16 contains a mixture of inclusions from 20-200 μm in size, and numerous elongated voids (Figure 4.4). A few large voids cross-cut the dominant orientation, possibly remnants from where two coils were joined in the wall of the vessel. The heterogeneous mineral grains in Sample 17 range from 20-500 μm, and the vessel contains laminar voids that do not show strong directionality (Figure 4.5). A few large voids do not follow the same pattern, forming large holes in the vessel body.

Sample 18 contains grain sizes ranging from 15-200 μm (Figure 4.6). Both laminar and amorphous void types are visible, and most show some degree of directionality. Inclusions in Sample 19 show very little variation in size, from approximately 5-20 μm (Figure 4.7). Again, a mixture of laminar and amorphous voids are present. Finally, grain sizes in Sample 25 are very heterogeneous, ranging from 60-600 μm, and voids are almost exclusively elongated in a single direction (Figure 4.8).

Variation can be observed in grain sizes and fabric textures between different vessels. Vessels can be divided into three groups based on the range of inclusion grain
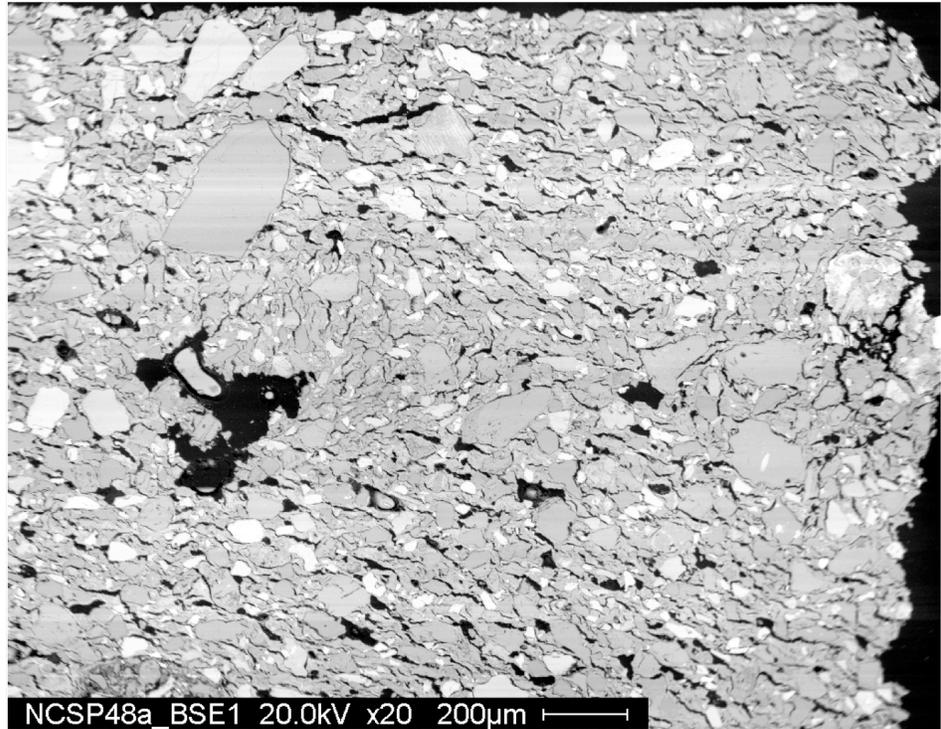
Figure 4.5 BSE-SEM image of vessel Sample 17.
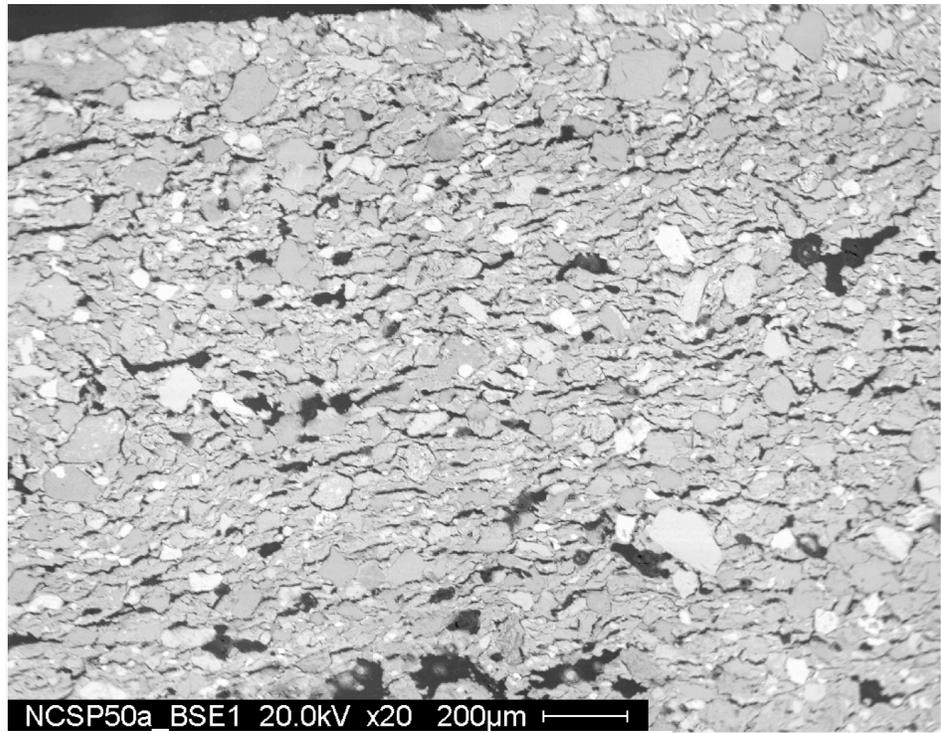
Figure 4.6 BSE-SEM image of vessel Sample 18.
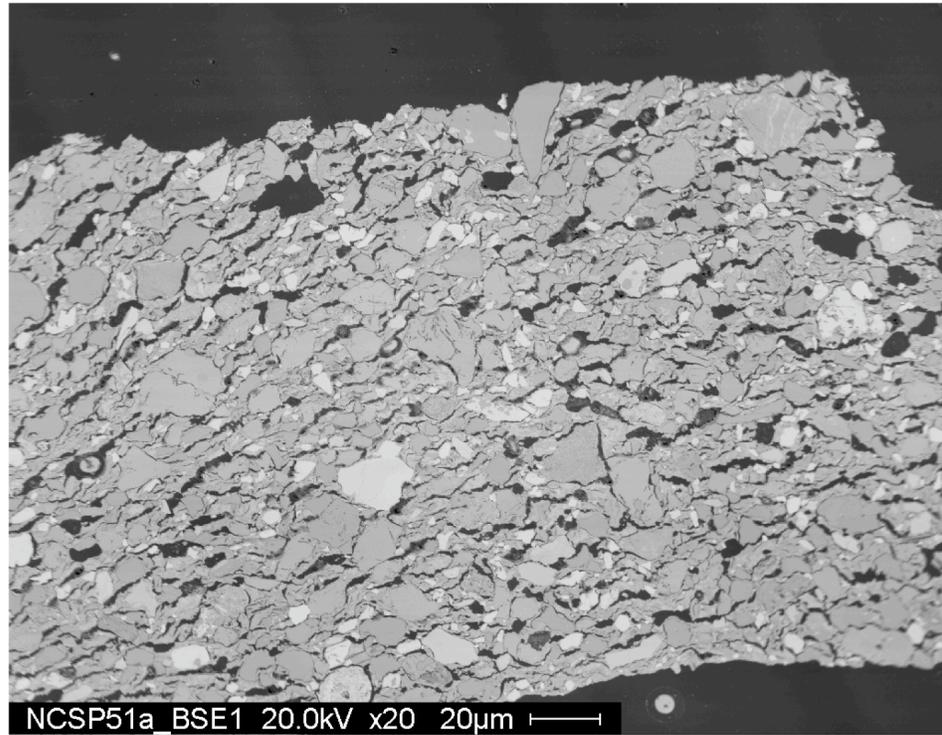
Figure 4.7 BSE-SEM image of vessel Sample 19.
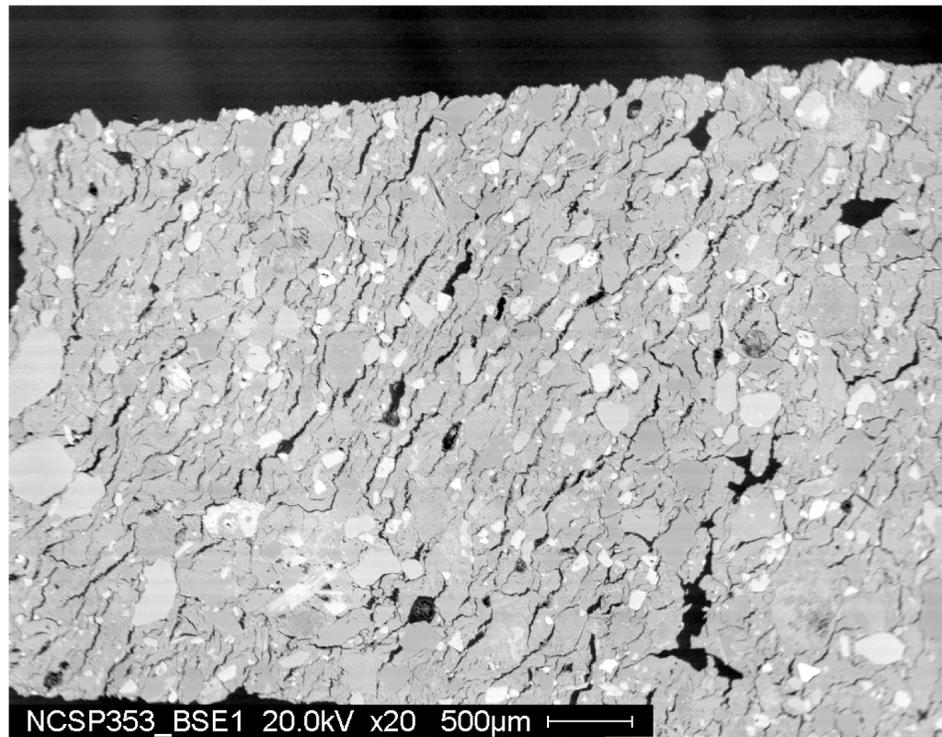
Figure 4.8 BSE-SEM image of vessel Sample 25.

Table 4.2 The variation of void shapes and inclusion sizes in vessel samples.

Group	Sample #	Void Shape	Inclusion Sizes (µm)	Inclusion Size Range (µm)	Homestead
1	15	laminar	5 - 45	<100	Salakahle
	19	laminar	5 - 20	<100	Zibuse
2	13	amorphous	25 - 300	100 - 300	Salakahle
	16	laminar	20 - 200	100 - 300	Salakahle
	18	laminar	15 - 200	100 - 300	Zibuse
3	14	amorphous	100 - 600	400 - 600	Salakahle
	17	laminar	20 - 500	400 - 600	Zibuse
	25	laminar	60 - 600	400 - 600	Salakahle

sizes they contain (Table 4.2). Group one (Samples 15 and 19) contains vessels with a very small range of inclusion size variation, less than 100 μm in total. The grain size variation of vessels in group two (Samples 13, 16 and 18) is between 100 and 300 μm. Group three (Samples 14, 17 and 25) contains vessels with heterogeneous grain sizes, their total range falling between 400 and 600 μm. This variation suggests that all clays are not necessarily processed in exactly the same way, allowing grain size to fluctuate. This type of variation in processing and forming techniques has been observed elsewhere (Gosselain 1998, 2008b; Livingstone Smith 2000), suggesting that there is a high tolerance for variation in ceramic production. Thus, all clays and vessels in a region will not necessarily be prepared and formed in the same way, resulting in discernible differences in physical structure, despite the same processing techniques being used. However, there does not appear to be a strong correlation between the range of grain sizes and the homestead in which vessels were produced. There is also no strong relationship between the clay source that is dominant in a vessel and its range of grain sizes. Although it is clear that there is some variability in the physical characteristics of vessels, that variability cannot be definitively explained using the data available in this study. It is possible, however, that variation might be related to the skill level of potters, and the time spent preparing batches of clay.

The results of bulk mineralogical analysis using XRD are generally consistent with the mineral identifications achieved using SEM. Quartz and feldspars are abundant in nearly all samples, and a small number of samples contain more unique minerals (Table 4.3, also see Appendix B). Both the raw black clay from *Siqumama*

Table 4.3 Results of XRD analysis.

Analytical Sample #	Sample Type	Processing Stage	Source Name	XRD Results
1	clay	unprocessed	Siqumama	quartz, albite, calcite (?)
2	clay	ground & sifted	Siqumama	quartz, albite
3	clay	ground, sifted & mixed	Siqumama & Nokhona	quartz, albite, enstatite (?)
4	clay	mixed nonplastics	Siqumama & Nokhona	quartz, albite
5	clay	mixed nonplastics	Siqumama & Nokhona	quartz, albite
6	clay	ground, sifted & mixed	Siqumama & Nokhona	quartz, albite, plagioclase, zircon (?)
7	clay	unprocessed	Nokhona	quartz, albite, orthoclase, microcline (?)
8	clay	nonplastics	Nokhona	n/a (ICP-MS only)
9	clay	ground & sifted	Nokhona	quartz, albite, microcline (?)
10	clay	unprocessed	Ntontonto	quartz, albite, kyanite (?)
11	clay	ground & sifted	Ntontonto	quartz, albite, calcite, anorthite (?)
12	clay	nonplastics	Ntontonto	quartz, albite
13	vessel	fired	Siqumama & Nokhona	quartz, albite, tremolite (?)
14	vessel	fired	Siqumama & Nokhona	quartz, albite
15	vessel	fired	Siqumama & Nokhona	quartz
16	vessel	fired	Siqumama & Nokhona	quartz, kyanite (?), ilmenite (?)
17	vessel	fired	Siqumama & Nokhona	quartz, albite, biotite, kyanite (?)
18	vessel	fired	Siqumama & Nokhona	quartz, albite, kyanite (?), anorthite (?)
19	vessel	fired	Siqumama & Nokhona	quartz, albite, biotite
20	clay	ground & sifted	Ntontonto	quartz, albite
21	clay	unprocessed	Ndondondwane	quartz
22	clay	ground & sifted	Ndondondwane	quartz, albite
23	clay	nonplastics	Ndondondwane	quartz, apatite (?)
24	river clay	unprocessed	river clay	quartz, albite, muscovite (?)
25	vessel	fired	Ndondondwane & Nokhona	quartz, albite, biotite (?)
26	clay	ground	Ndondondwane	quartz, albite, microcline (?)
27	clay	nonplastics	Siqumama	quartz, albite, calcite

(Sample 1) and the nonplastics removed during sifting (Sample 27) contain quartz, albite and calcite. Only quartz and albite are identifiable for the sifted clay from *Siqumama* (Sample 2).

The analysis of raw black clay from *Ndondondwane* (Sample 21) reveals only quartz, but the sifted clay (Sample 22) also contains albite, and the nonplastics (Sample 23) appear to contain apatite. The clay sample collected in 2002 (Sample 26), reported to be from *Ndondondwane*, contains quartz, albite and possibly microcline. Raw and processed red clay from *Nokhona* (Samples 7 and 9) contain quartz, feldspar (albite and orthoclase), and possibly microcline, which appears to be unique to this source. All red clay samples from *Ntontonto* (Samples 10-12, 20) contain quartz and albite, but the raw clay (Sample 10) may also contain kyanite, and the sifted clay (Sample 11) appears to contain calcite and anorthite. Finally, the unprocessed river clay (Sample 24) contains quartz, albite, and possibly muscovite.

Mixed clays from *Siqumama* and *Nokhona* (Samples 3-6) contain quartz, albite and plagioclase, with possible identifications for enstatite and zircon (Table 4.3). Aside from quartz and albite, the minerals identified in the mixed clay samples are not accounted for in samples from either source. This does not mean that these minerals are absent from the clays, only that they could not be identified using XRD.

Although the majority of finished vessels contain the same mixture of clays from *Siqumama* and *Nokhona*, different minerals were identified in some of the vessel samples. Only quartz could be identified in Sample 15, and quartz and albite in Sample 14. Sample 13 contains quartz, albite and possibly tremolite. In addition to
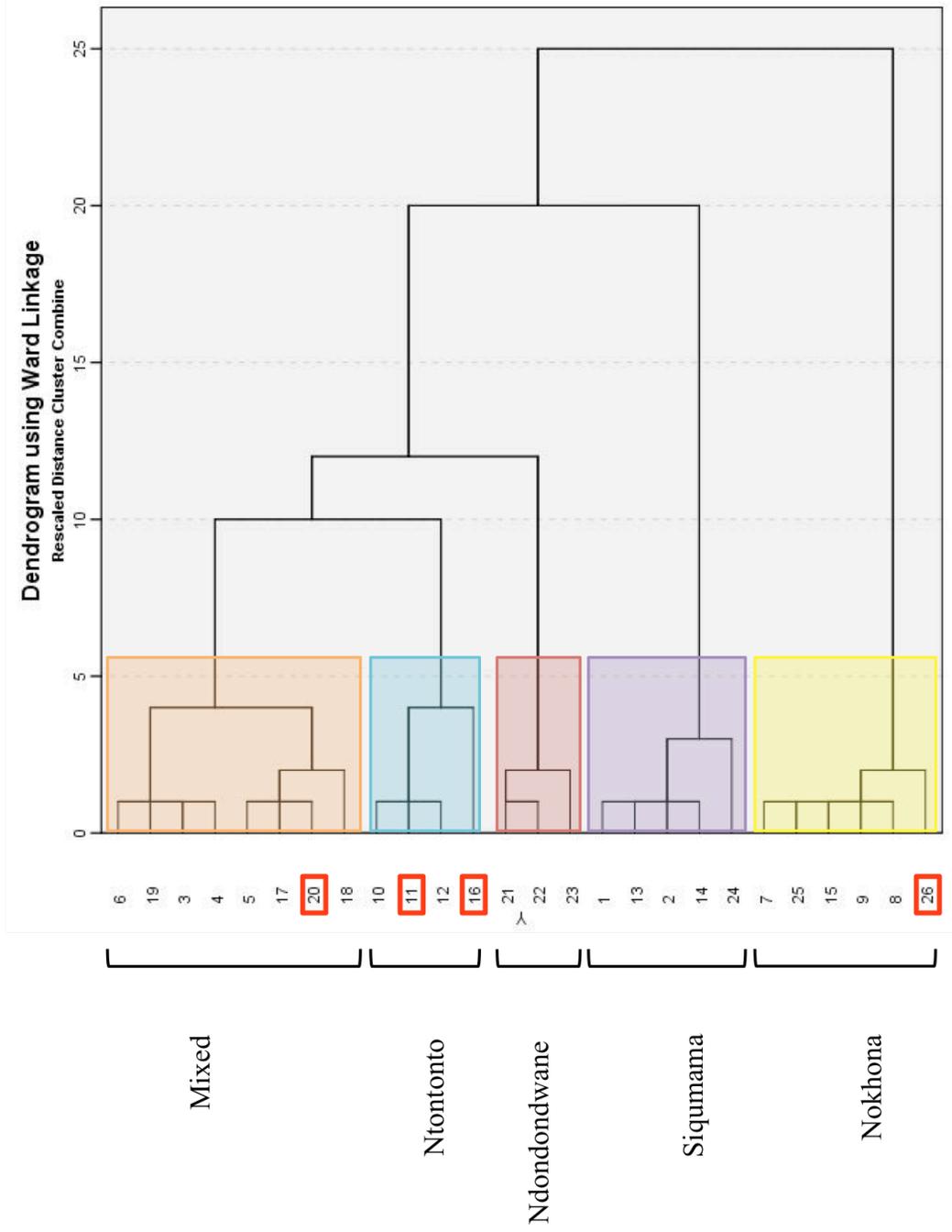
Figure 4.9 Cluster analysis of all samples using Ward Linkage. Five compositional groups are highlighted. Samples outlined in red are discussed individually.

quartz, Sample 16 may contain kyanite and ilmenite. Sample 17 contains quartz, albite and biotite, and possibly kyanite. Sample 18 contains quartz and albite, and may contain kyanite and anorthite. Sample 19 contains quartz, albite and biotite. The vessel collected in 2002 (Sample 25), which was reported to contain clays from *Ndondondwane* and *Nokhona,* contains quartz and biotite, and may contain microcline. Microcline was also identified in samples from *Nokhona*, and its presence in Sample 25 may be attributed to the use of clay from that source.

More detailed compositional profiles could not be obtained using XRD due to the complex mineralogy of the samples, which causes individual minerals to be lost in the complete spectra. The high concentration of quartz in many samples also tends to mask other peaks in the XRD spectra. Although some minerals are only identified in a few samples (for example, enstatite and zircon in mixed clay Samples 3 and 6) it is likely that they are present in other samples but could not be accurately identified. This "masking effect" (Kodama, et al. 1989) makes it problematic to draw any clear conclusions about provenance from the XRD data.

4.2 Results of Chemical Analysis

Cluster analysis revealed five broad compositional groups in the data. These groups establish good separation between clay sources, with raw and processed clays being grouped together. About half of the vessels were associated with particular clay sources, and the other half were included with mixed clay samples (Figure 4.9).

The first group contains mixed clays (both sifted clays and nonplastics), as well as three finished vessels (Samples 17, 18 and 19). This group also contains a sample of processed clay from *Ntontonto* (Sample 20), and this misclassification will be

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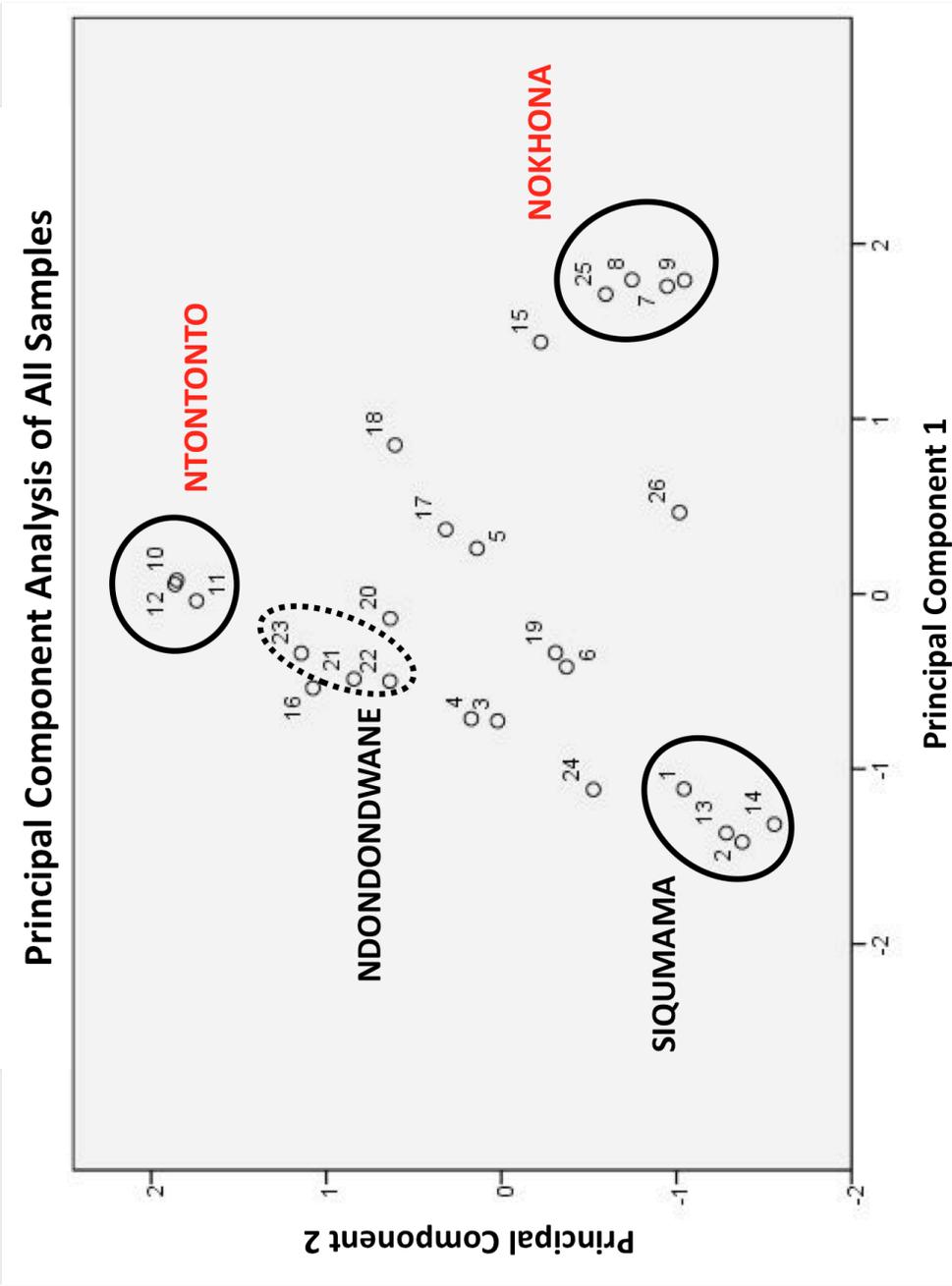
Figure 4.10 Principal component analysis of all samples. Ellipses illustrate compositional clusters, and have no statistical significance. Dotted line delineates clays from a single source which do not form a distinct cluster. Text colour signifies clay type, red or black.

discussed in Section 4.3. The second group contains clays from *Ntontonto* and one vessel (Sample 16). Group three contains only clays from *Ndondondwane*. Group four contains clays from *Siqumama*, two vessels (Samples 13 and 14), and river clay (Sample 24). The last group consists of clays from *Nokhona*, two vessels (Samples 15 and 25), and *Ndondondwane* clay collected in 2002 (Sample 26).

Similar results were obtained using PCA, although the clearest compositional groups are produced by three clay sources (*Siqumama*, *Nokhona* and *Ntontonto*), with a few individual vessels strongly associated with the raw clays (circled groups in Figure 4.10). Mixed clay samples, remaining vessels and clays from *Ndondondwane* (Samples 21, 22, 23) are located near the centre of the biplot.

4.2.1 Chemical Composition of Clay Sources

Although the characteristic composition of each source is best assessed using PCA, cluster analysis provides some information about the relative similarity between different clays. The most closely related raw clays are the black clay from *Siqumama* and the river clay (Figure 4.11). Although the precise source location for the river clay is not known, it is likely that it was obtained along the Nsuze River (Fowler, personal communication). The seasonal stream along which *Siqumama* is located drains into the Nsuze, which could explain the similar composition of these clays. Red clay from *Ntontonto* and black clay from *Ndondondwane* have some compositional similarities which lead to them being clustered together. The red clay source *Nokhona* is compositionally distinct from each of these clusters.
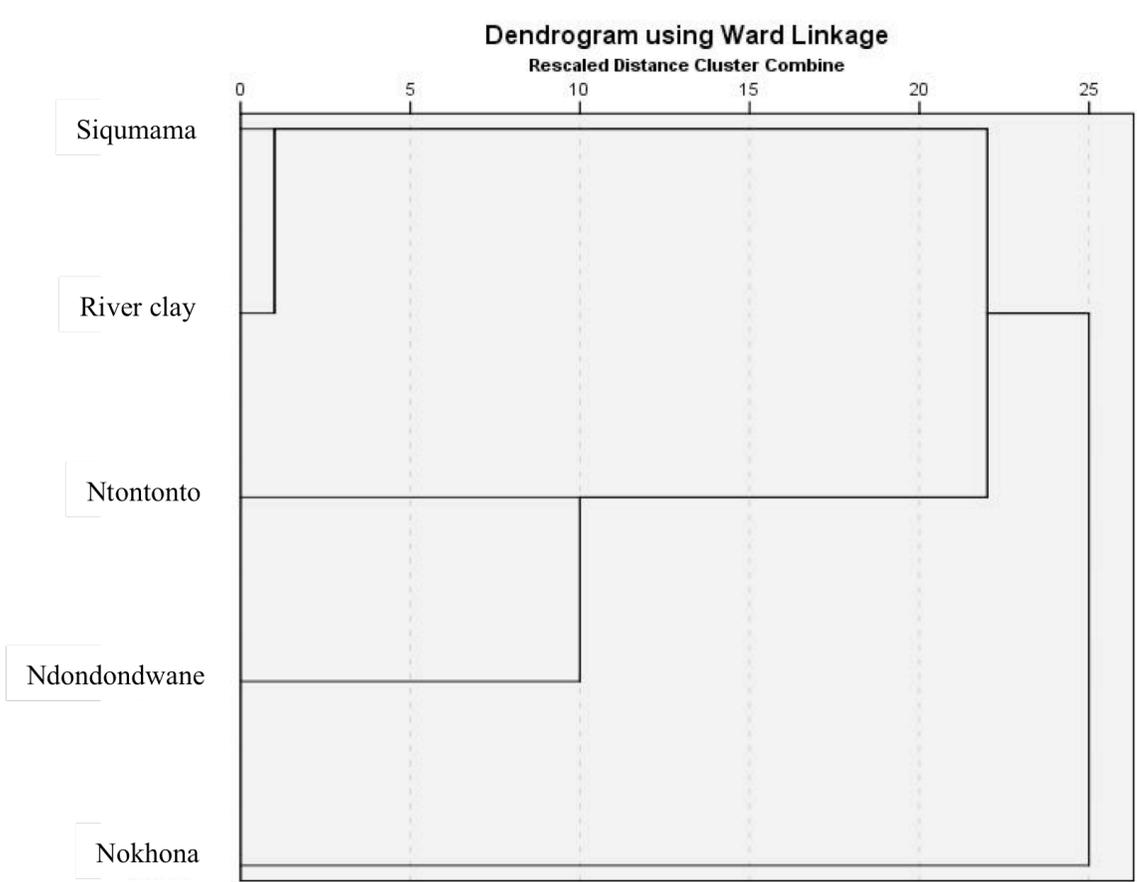
Figure 4.11 Cluster analysis of raw clay samples.

Figure 4.12 Principal component element loadings.

Significant elements associated with each clay source are defined by comparing the component loadings depicted in Figure 4.12 with the element concentrations observed for each sample. Components that strongly affect the distribution of clay sources in the PCA biplot that occur in uniquely high amounts at individual sources are considered characteristic. Black clay from *Siqumama* is characterized by high levels of sodium oxide (Na_2O) and strontium (Sr) (Figure 4.13, see list of samples in Table 4.4). Red clay from *Nokhona* is best characterized by high concentrations of potassium oxide (K_2O), lanthanum (La), cerium (Ce) and thorium (Th), and low levels of nickel (Ni) and chromium (Cr) (Figure 4.13). Clay from *Ntontonto* can be characterized by high levels of Cr, Ni and zirconium (Zr) (Figure 4.13). Black clay from *Ndondondwane* is distinguished by high concentrations of phosphorus pentoxide (P_2O_5) and zinc (Zn), and low levels of Na_2O (Figure 4.13). When all clay and vessel samples are included in the analysis (Figure 4.10), *Ndondondwane* is clustered alongside the mixed clay and vessel samples, close to clays from *Ntontonto*, which have similar compositional profiles. Although the raw and processed clays from *Ndondondwane* (Samples 21-23) group together, they do not form a cluster that is as distinct as those associated with the other clay sources.

Table 4.4 List of raw clay samples.

Sample Number	Sample Type	Clay Source Name
1	black clay	Siqumama
7	red clay	Nokhona
10	red clay	Ntontonto
21	black clay	Ndondondwane
24	river clay	n/a

Figure 4.13 Principal component analysis of raw clay sources.

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4.2.2 Chemical Composition of Processed Clays

Processed clays that have been ground and sieved are strongly associated with raw clays when they are derived from a single source, as are the nonplastics removed from those clays (Samples 1 and 2, 7-9, 10-12, and 21-23, Figure 4.10). Processed clays and nonplastics that have been mixed with clay from another source (Samples 3-6) do not cluster near a single source, but are distributed in the centre of the biplot. The mixture of different elements contained in these samples results in their location near the centre of the biplot, and their relationship to either source is not made apparent using principle components.

Cluster analysis of clay samples helps to identify the relationship between raw clay and mixed clays, but only with regards to the dominant clay type in the mixture. In the dendrogram, mixed clays (Samples 3-6) are most closely related to raw and processed clay from *Siqumama* (Samples 1 and 2, Figure 4.5). Although potters describe their clay mixtures as approximately equal proportions of each clay, in reality one clay may be over-represented. The position of mixed clays in the cluster analysis suggest that raw clay from *Siqumama* is represented in higher proportions than *Nokhona*. Therefore, although it is not possible to identify the other source that was used to create this mixture using cluster analysis, the association of mixed clays with *Siqumama* would allow the provenance of these clays to be determined with some degree of accuracy.

The same effect is likely responsible for the unexpected composition of the sample of *Ndondondwane* clay collected from the potters in 2002 (Sample 26). This sample was recorded as a pure black clay sample, but it does not cluster with the
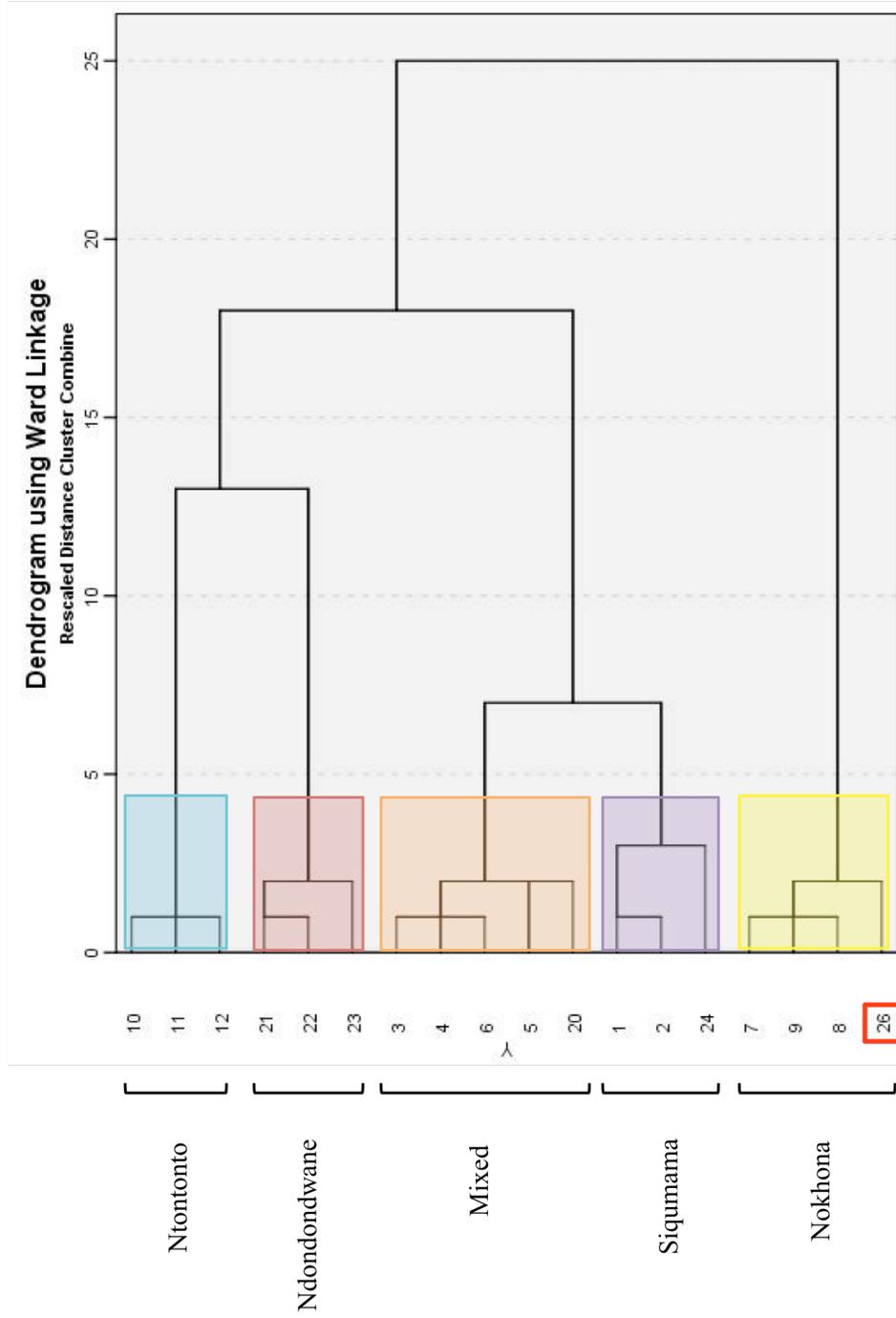
Figure 4.14 Cluster analysis of raw and processed clays using Ward Linkage. Compositional groups are highlighted. Sample 26, reported to be composed of black clay from *Ndondondwane*, clusters with red clays from *Nokhona*.

other clays derived from the same source (Samples 21-23). On the PCA biplot this sample is loosely associated with raw and processed clays from *Nokhona* (Figure 4.10). The same relationship is represented in the cluster analysis (Figure 4.14). It appears that Sample 26 is in fact a mixed clay, and the major proportion of this mixture seems to derive from *Nokhona*. As with the other mixed samples, it would be possible to correctly conclude that this clay is from a source in Nkandla, it would not be obvious that the sample contains a mixture of clays from two distinct sources.

One processed clay sample that is not strongly associated with raw and processed clays from the same source is the sifted clay from *Ntontonto* (Sample 20). This sifted clay sample was collected directly from potters, and a duplicate (Sample 11) was manufactured in the lab in order to obtain a sample of nonplastics from the raw clay. Since these two samples are both associated with clay from *Ntontonto*, they would be expected to have similar chemical compositions. For all other sources, raw and processed clays are strongly associated in both cluster analysis and PCA. Instead, Sample 20 is associated with mixed, processed clays from *Siqumama* and *Nokhona*. In the PCA biplot (Figure 4.10), Sample 20 is closely associated with clays from *Ndondondwane*, which shares some features with *Ntontonto*.

The compositional differences that separate Sample 20 from other clays from the same source may be the result of natural variability within the clay source itself. The two other processed clays (Samples 11 and 12) from *Ntontonto* were all produced from the same sample of raw clay. Sample 20 was ground by potters from another batch of raw clay collected from the same source. These two samples of raw clay may have been collected from different areas within the same source, and since the degree of

compositional variation within each source is not documented it is possible that these samples represent the compositional extremes naturally present at *Ntontonto*.

Another possible explanation for the composition of this sample has to do with resource procurement behaviour. Sample 11 was collected directly from the raw clay source, with a potter pointing out the appropriate stratum, whereas Sample 20 was produced using clay from the potter's stockpile. Potters often send their children to collect clay, and children may not be as familiar with the distinctions between clay and soil strata. *Ntontonto* is located in an area that often experiences soil slumping after rains, and if children collected clay without first clearing away slumped topsoil, the sample would have a different composition from the pure red clay associated with this source.

4.2.3 Chemical Composition of Finished Vessels

The patterns previously discussed regarding the composition of mixed clays are also important when considering the composition of finished vessels. The composition of all vessels collected in Nkandla was reported by potters to be a mixture of clay from *Siqumama* and *Nokhona*. PCA analysis of all samples reveals that there is some variation in the relative proportion of each clay used to produce these vessels. Samples 13 and 14 are very strongly associated with raw and processed clay from *Siqumama* (Samples 1 and 2, Figure 4.10). Samples 17, 18 and 19 are spread out in the central portion of the PCA biplot, similar to the samples of mixed clay. The vessel collected in 2002 (Sample 25) is associated with raw and processed clays from *Nokhona*. Sample 15 is also loosely related to clays from *Nokhona*.

The same relationships can be seen when cluster analysis is performed using all samples (Figure 4.9). Samples 13 and 14 are grouped with clay from *Siqumama*, and
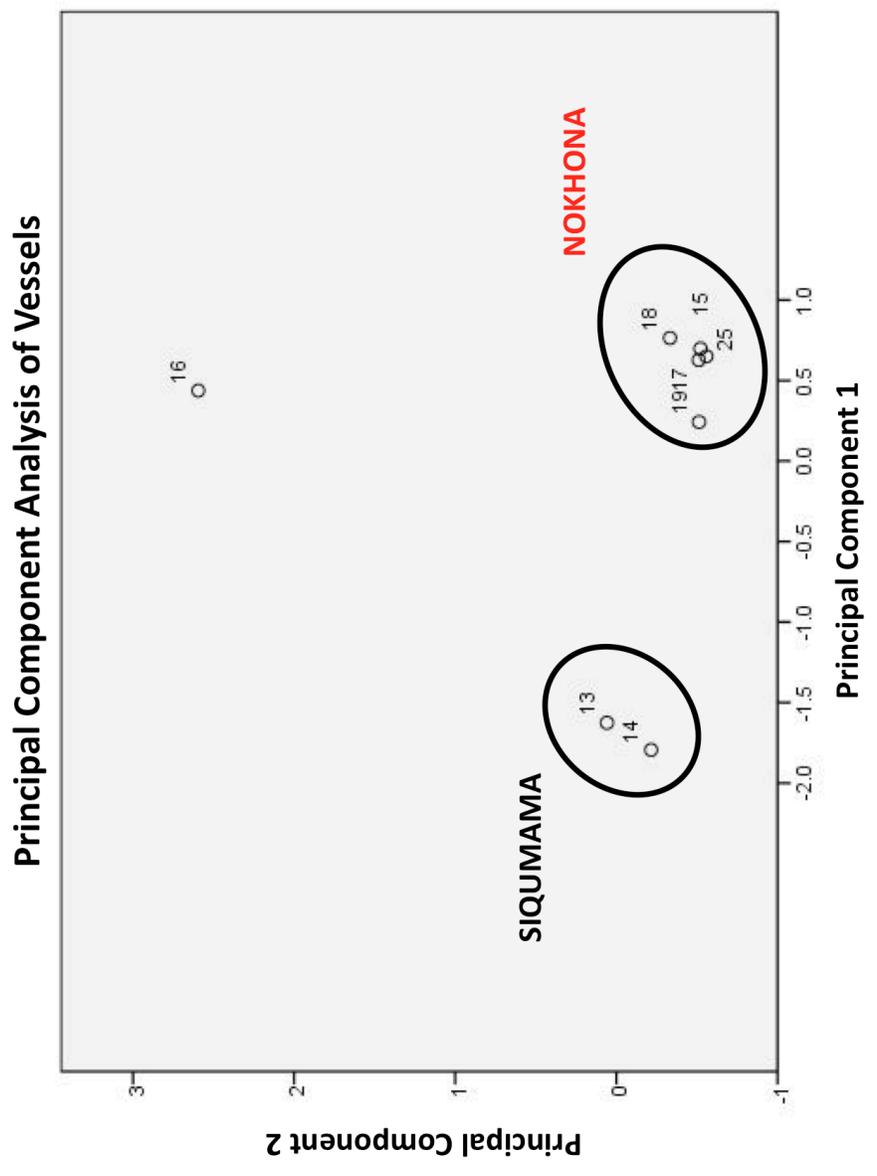
Figure 4.15 Principal component analysis of vessels. Ellipses illustrate compositional groups and do not have statistical significance. Text colour denotes dominant clay type, red or black.

Samples 15 and 25 are clustered with clays from *Nokhona*. Samples 17, 18 and 19 are associated with mixed clays from *Siqumama* and *Nokhona*, which suggests that these vessels conform most closely to the potters' reported mixture of equal proportions of clay from each source. However, as discussed with the mixed clays, the next level of agglomeration is a group of mixed clays and vessels with samples associated with *Siqumama*. Cluster analysis of all samples would seem to suggest that Samples 17, 18 and 19 derive from *Siqumama* clays, as that appears to be the major constituent of the mixture (although not to the same degree as in Samples 13 and 14).

The compositional variation between vessels, and the association of particular vessels with raw clay sources, becomes clearer when analyses are performed using a subset of samples. PCA of vessel samples reveals three compositional groups (Figure 4.15). Samples 13 and 14 maintain the same position that they did when all samples were included, and although Samples 15, 16 and 25 is altered slightly, they remain in the same general area as before (Figure 4.10). The most revealing change when clay samples are excluded is in the position of Samples 17, 18 and 19. In the original biplot these vessel samples were located in the centre of the biplot, along with samples of mixed clays. These samples were too dissimilar to clays representing each single source to be grouped nearby. However, in the biplot of vessels alone, Samples 17, 18 and 19 cluster very nicely with Samples 15 and 25, both of which have been shown to be associated with clay from *Nokhona*. The implication is that although the proportion of black clay is high enough in these vessels to disassociate them from *Nokhona* clays, red clay from *Nokhona* is a major component in the vessels.
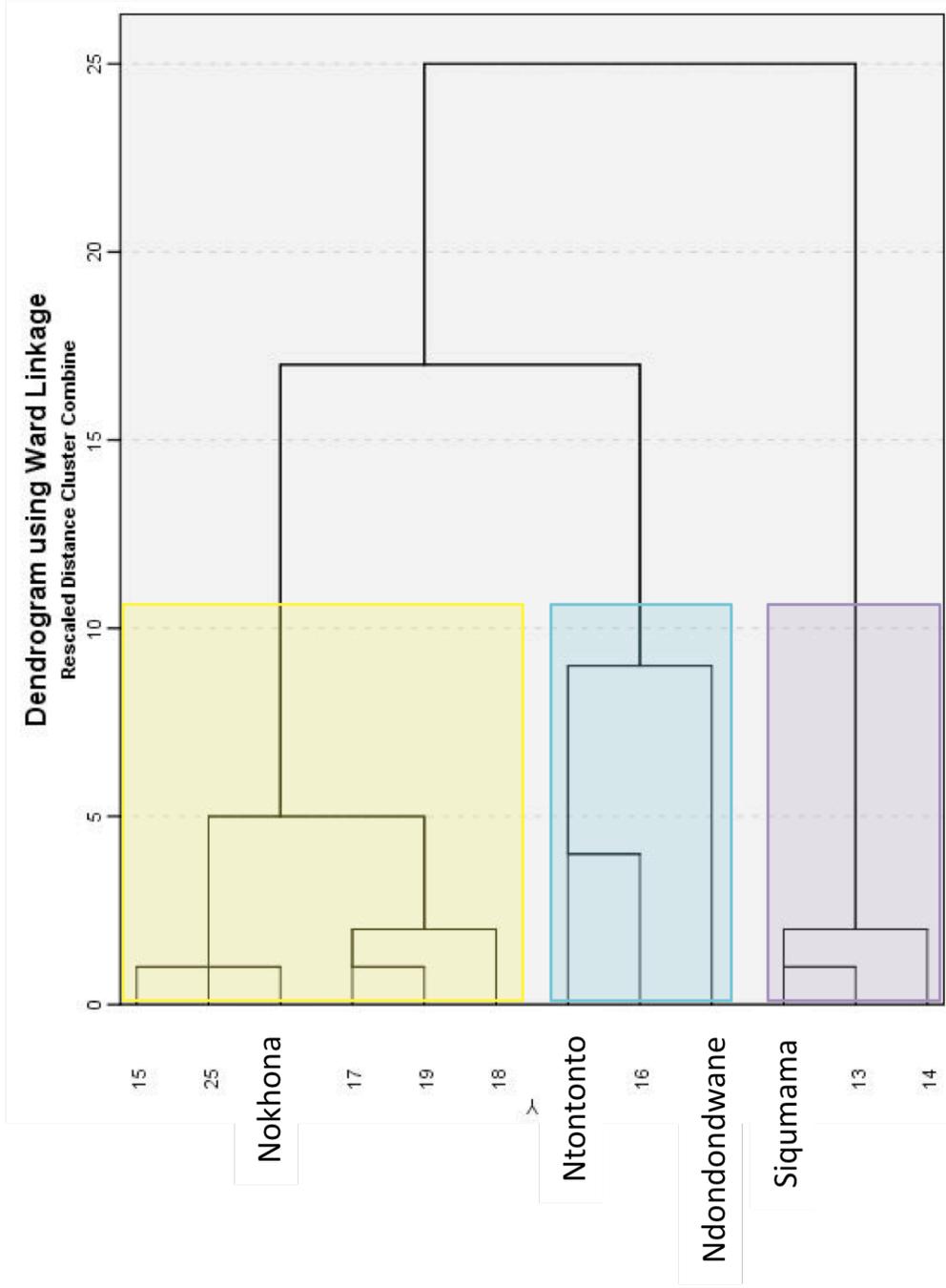
Figure 4.16 Cluster analysis of vessel samples and raw clay sources using Ward Linkage. Relevant clusters are highlighted.
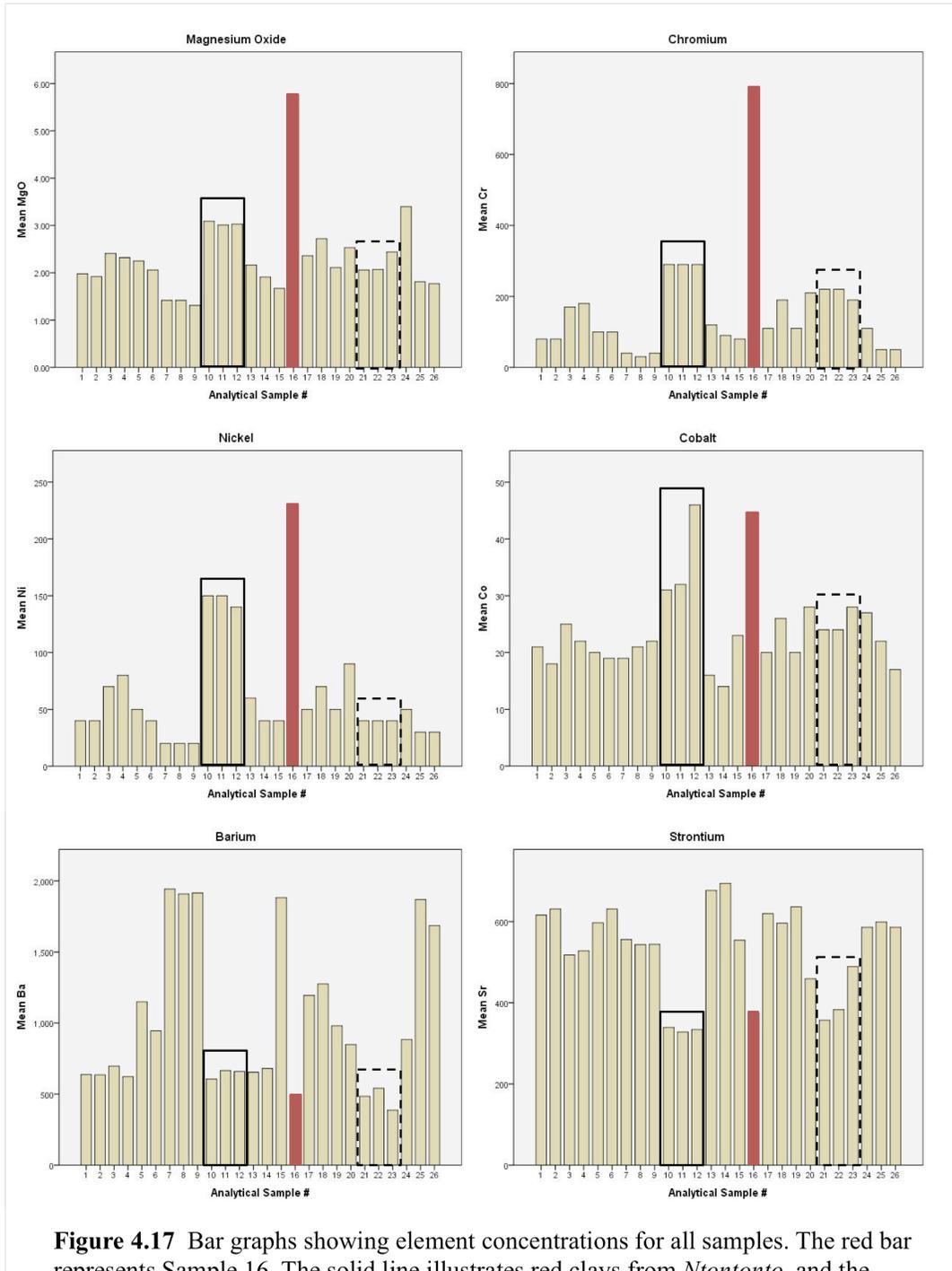
Figure 4.17 Bar graphs showing element concentrations for all samples. The red bar represents Sample 16. The solid line illustrates red clays from *Ntontonto*, and the dashed line illustrates black clays from *Ndondondwane*.

This conclusion is borne out by the cluster analysis of vessel samples along with raw clays (Figure 4.16). Samples 25 and 15 are immediately clustered with raw clay from *Nokhona* (Sample 7), and at the next level of agglomeration they are grouped with Samples 17, 18 and 19. From the combined results of PCA and cluster analysis it can be inferred that these vessels are more similar to clay from *Nokhona* than they are to black clay from *Siqumama* (Sample 1) or *Ndondondwane* (Sample 21).

The final vessel, represented by Sample 16, is an outlier compared with the other vessels. Its position on the original biplot suggests that there is little similarity between this vessel and the clays from which it was manufactured (Figure 4.10). In fact, its location implies a closer relationship to clays from *Ntontonto* and *Ndondondwane*. The separate analysis of vessels also distances Sample 16 from the other vessel samples (Figure 4.15). This outlying sample warrants some additional consideration.

During preliminary analysis using dot-plots, Sample 16 began to stand out as an outlying value. Concentrations of magnesium oxide (MgO), chromium (Cr), cobalt (Co) and nickel (Ni) are high compared with other samples (Figure 4.17), although in all cases the next highest levels occur in clays from *Ntontonto* (Samples 10-12). Clays from *Ndondondwane* (Samples 21-23) also display high levels of Cr. Levels of barium (Ba) and strontium (Sr) are much lower than average in Sample 16. Similarly low levels of Ba are present at *Ndondondwane*, and of Sr at *Ntontonto* and *Ndondondwane*.

These similarities in composition explain why Sample 16 is proximate to clays from *Ndondondwane* and *Ntontonto* in the original PCA biplot (Figure 4.10).

Table 4.5 The concentration of Ba and Ni in raw clays and vessels (see Figure 4.18).

Sample Number	Source(s)	Processing Stage	Ba (ppm)	Ni (ppm)
1	Siqumama	unprocessed	637	40
7	Nokhona	unprocessed	1944	20
10	Ntontonto	unprocessed	606	150
13	Siqumama, Nokhona	fired	654	60
14	Siqumama, Nokhona	fired	680	40
15	Siqumama, Nokhona	fired	1883	40
16	Siqumama, Nokhona	fired	492	230
17	Siqumama, Nokhona	fired	1195	50
18	Siqumama, Nokhona	fired	1275	70
19	Siqumama, Nokhona	fired	980	50
21	Ndondondwane	unprocessed	485	40
24	Nsuze River	unprocessed	884	50
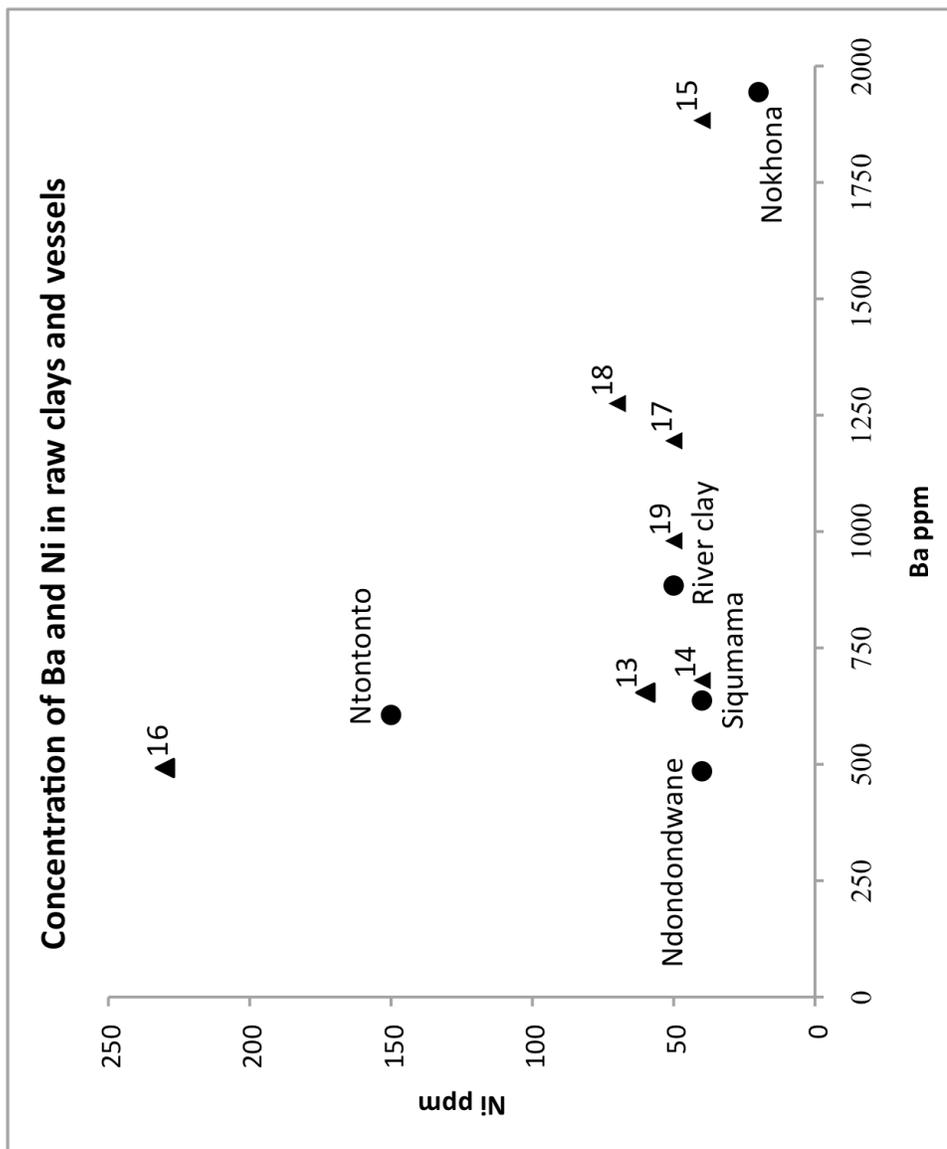
Figure 4.18 The concentration of Ba and Ni in raw clays and vessels (see Table 4.5). Note high levels of Ni in Sample 16 and clay from *Ntontonto*. Circles represent raw clay samples, triangles represent vessel samples.

Cluster analysis of vessels and raw clays associates Sample 16 with clays from *Ntontonto* (Figure 4.16). If the mixing effect seen with other vessels is responsible for these patterns, it suggests that Sample 16 is primarily composed of clay from *Ntontonto*.

The relationship between Sample 16 and the red clay sources can be clarified by comparing the concentrations of barium (Ba) and nickel (Ni) in raw clays and vessel samples (see Figure 4.18 and Table 4.5). These elements were selected for comparison based on their high standard deviation, and because they clearly separate the red clay sources. *Nokhona* clay contains high levels of Ba and low levels of Ni, whereas clay from *Ntontonto* is Ni-rich and low in Ba. Sample 16 has very high levels of Ni, and low levels of Ba. The presence of red clay from *Ntontonto* is the only possible explanation for the abundance of Ni in Sample 16 – no other raw clay contains a significant amount of Ni. This element plot does not clarify whether the black clay in the mixture is from *Siqumama* or *Ndondondwane* because the two black clay sources have similar levels of Ba and Ni.

In the dendrogram of raw clays and vessels (Figure 4.16), the raw red clay from *Ntontonto* and Sample 16 are clustered with raw black clay from *Ndondondwane*. Although at first glance this appears to suggest that Sample 16 contains a mixture of these two clays, this conclusion may be problematic. As we saw in the PCA biplot (Figure 4.10) and the cluster analysis of clay sources (Figure 4.11), clays from *Ntontonto* and *Ndondondwane* share similarities in their chemical composition. These similarities are responsible for their aggregation in the dendrogram. A significantly different relationship is represented when Average Linkage is used to generate clusters (Figure
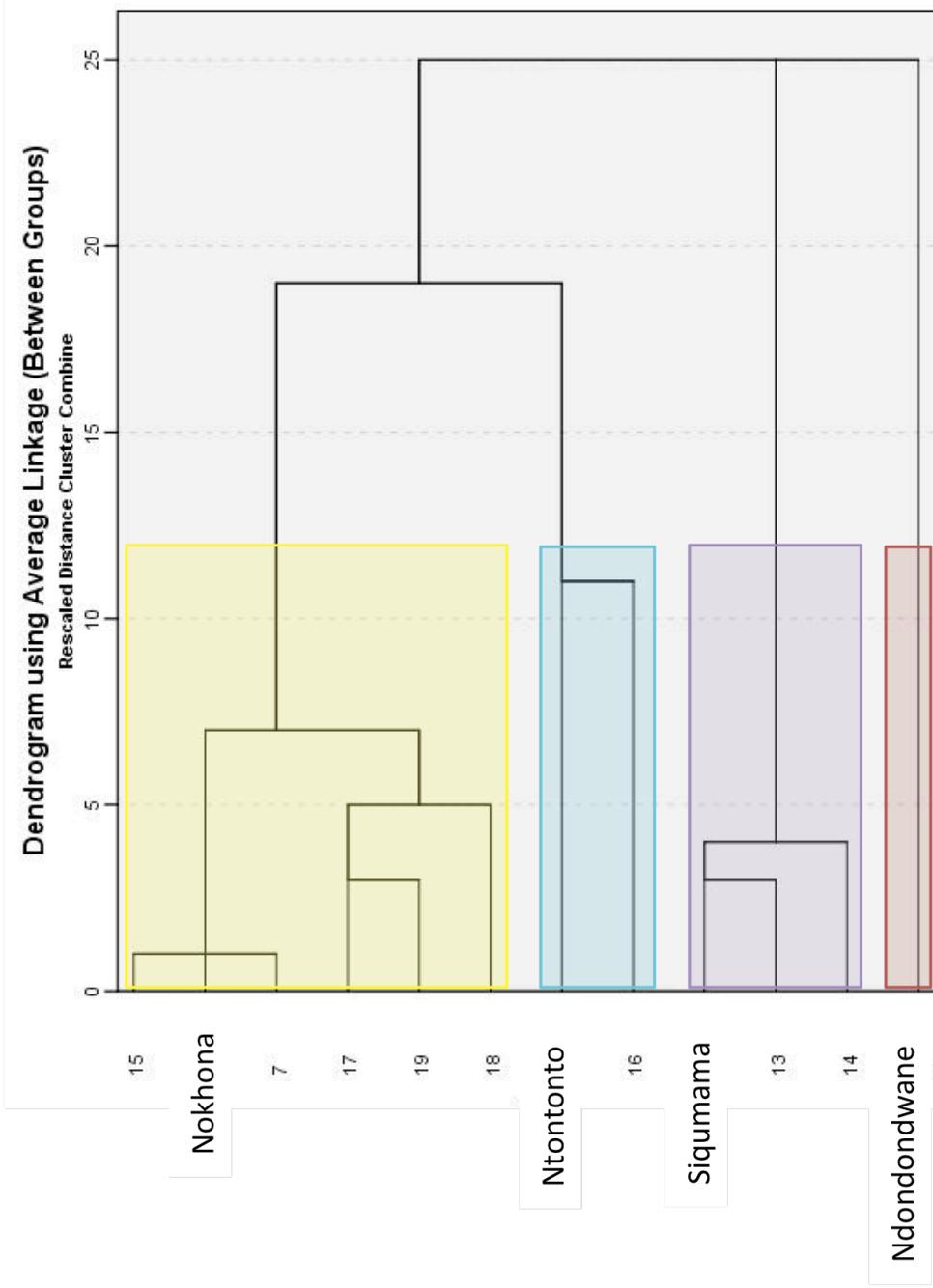
**Figure 4.19** Cluster analysis of vessel samples and raw clay sources using Average Linkage. Relevant clusters are highlighted. Note the position of raw clay from *Ndondondwane* compared with the dendrogram using Ward Linkage (Figure 4.16).

4.19). Ward Linkage groups all three samples together because of a few similar elements in their composition, which minimizes the total increase in variation when they are agglomerated. However, Average Linkage detects the many differences that exist in the total overall composition of these samples, and clay from *Ndondondwane* does not form a cluster with any other clays or vessels.

The composition of raw black clays is best distinguished using another pair of elements, sodium oxide (Na_2O) and zinc (Zn) (Table 4.6). When the ratios of these elements are compared, raw black clays from *Ndondondwane* and *Siqumama* are clearly separated (Figure 4.20). *Ndondondwane* clay contains high levels of Zn and a low concentration of Na_2O, whereas clay from *Siqumama* contains relatively low levels of Zn and higher concentration of Na_2O. Sample 16 contains moderate levels of both Zn and Na_2O. The concentration of Na_2O in Sample 16 could be due to the presence of red clay from *Ntontonto*, which also contains moderate amounts of this element, and does not conclusively indicate which black clay is a component of this vessel. The relatively low concentration of Zn, however, suggests that *Siqumama* is the black clay constituent in Sample 16.

Both *Ntontonto* and *Ndondondwane* display fairly high levels of Zn, and a mixture of the two would produce a vessel with a Zn concentration somewhere between the two clays. This concept of "mass balance" applies the principle of mass conservation, which states that mass cannot be created or destroyed, so the mass that enters a system will be equal to the mass that leaves the system or accumulates within the system. The effect of mixing clays can be seen in Figure 4.21 (also see Table 4.7), which shows the barium (Ba) and cerium (Ce) content of raw clays from *Siqumama* and *Nokhona*, as well

Table 4.6 The concentration of Na_2O and Zn in raw and processed clays and vessels (see Figure 4.20).

Sample Number	Source(s)	Processing Stage	Na$_2$O (%)	Zn (ppm)
1	Siqumama	unprocessed	3.23	60
2	Siqumama	ground & sifted	3.28	60
3	Siqumama, Nokhona	ground, mixed & sifted	2.84	70
4	Siqumama, Nokhona	mixed nonplastics	2.97	80
5	Siqumama, Nokhona	mixed nonplastics	2.48	70
6	Siqumama, Nokhona	ground, mixed & sifted	3.04	70
7	Nokhona	unprocessed	2.29	50
8	Nokhona	nonplastics	2.22	50
9	Nokhona	ground & sifted	2.37	50
10	Ntontonto	unprocessed	2.35	90
11	Ntontonto	ground & sifted	2.3	90
12	Ntontonto	nonplastics	2.4	90
13	Siqumama, Nokhona	fired	3.65	60
14	Siqumama, Nokhona	fired	3.7	50
15	Siqumama, Nokhona	fired	2.38	60
16	Siqumama, Nokhona	fired	2.17	70
17	Siqumama, Nokhona	fired	2.98	80
18	Siqumama, Nokhona	fired	2.68	80
19	Siqumama, Nokhona	fired	3.14	70
20	Ntontonto	ground & sifted	2.69	70
21	Ndondondwane	unprocessed	1.09	110
22	Ndondondwane	ground & sifted	1.24	120
23	Ndondondwane	nonplastics	0.9	110
24	Nsuze River	unprocessed	2.56	70
25	Ndondondwane, Nokhona	fired	2.52	60
26	Ndondondwane	ground	2.48	50
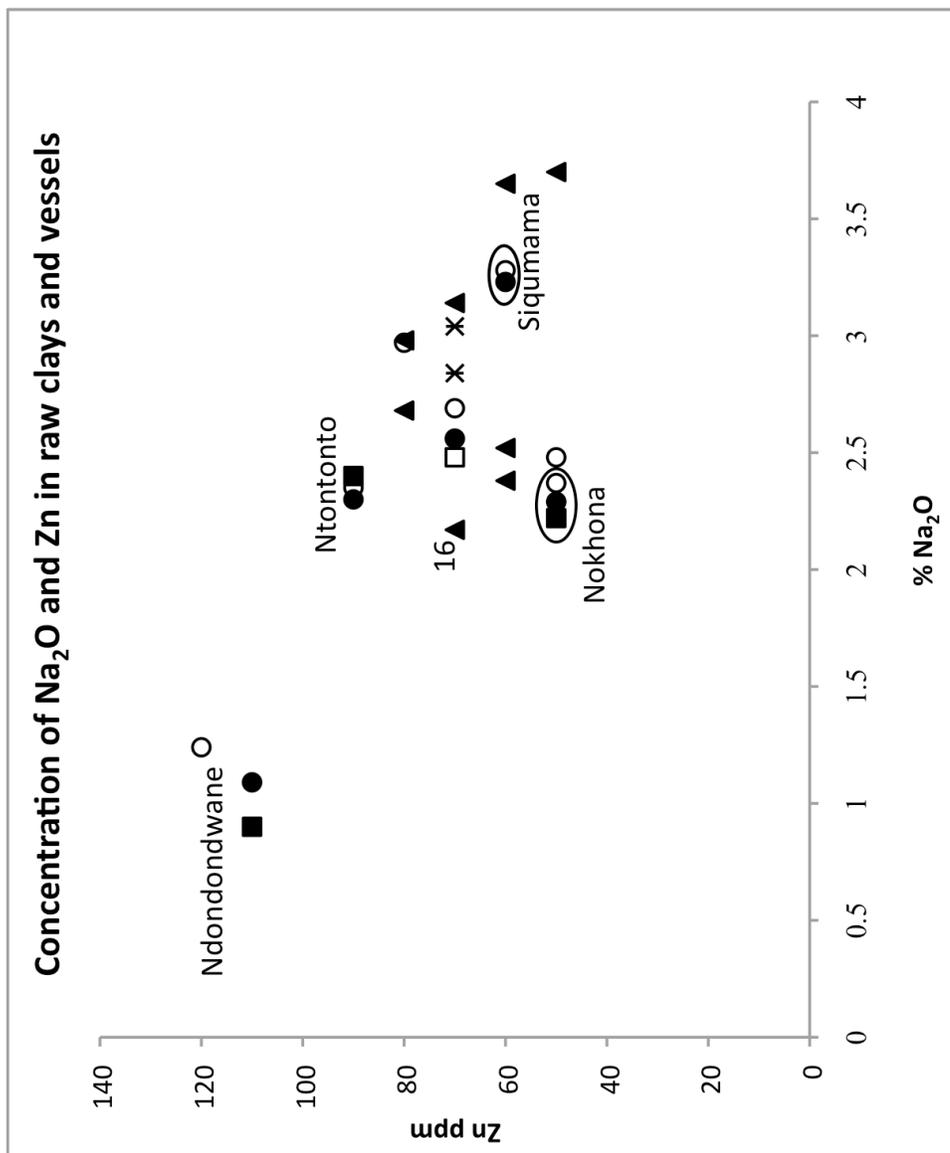
Figure 4.20 The concentration of Na_2O and Zn in raw and processed clays and vessels (see Table 4.6). Filled circles represent unprocessed clay, unfilled circles represent ground and sifted clay. Asterisks represent mixed processed clays. Filled squares represent nonplastics from a single source, unfilled squares represent mixed nonplastics, and triangles represent vessels.

Table 4.7 The concentration of Ba and Ce in raw and processed clays and vessels (see Figure 4.21).

| Sample #	Processing Stage	Source(s)	Ba (ppm)	Ce (ppm)
1	unprocessed	Siqumama	637	56.2
2	ground & sifted	Siqumama	635	50.4
3	ground, mixed & sifted	Siqumama, Nokhona	697	69
4	mixed nonplastics	Siqumama, Nokhona	622	65.3
5	mixed nonplastics	Siqumama, Nokhona	1150	113
6	ground, mixed & sifted	Siqumama, Nokhona	945	90.2
7	unprocessed	Nokhona	1944	178
8	nonplastics	Nokhona	1909	172
9	ground & sifted	Nokhona	1915	182
13	fired	Siqumama, Nokhona	654	48.9
14	fired	Siqumama, Nokhona	680	49.3
15	fired	Siqumama, Nokhona	1883	167
16	fired	Siqumama, Nokhona	492	75.2
17	fired	Siqumama, Nokhona	1195	115
18	fired	Siqumama, Nokhona	1275	128
19	fired	Siqumama, Nokhona	980	91.4
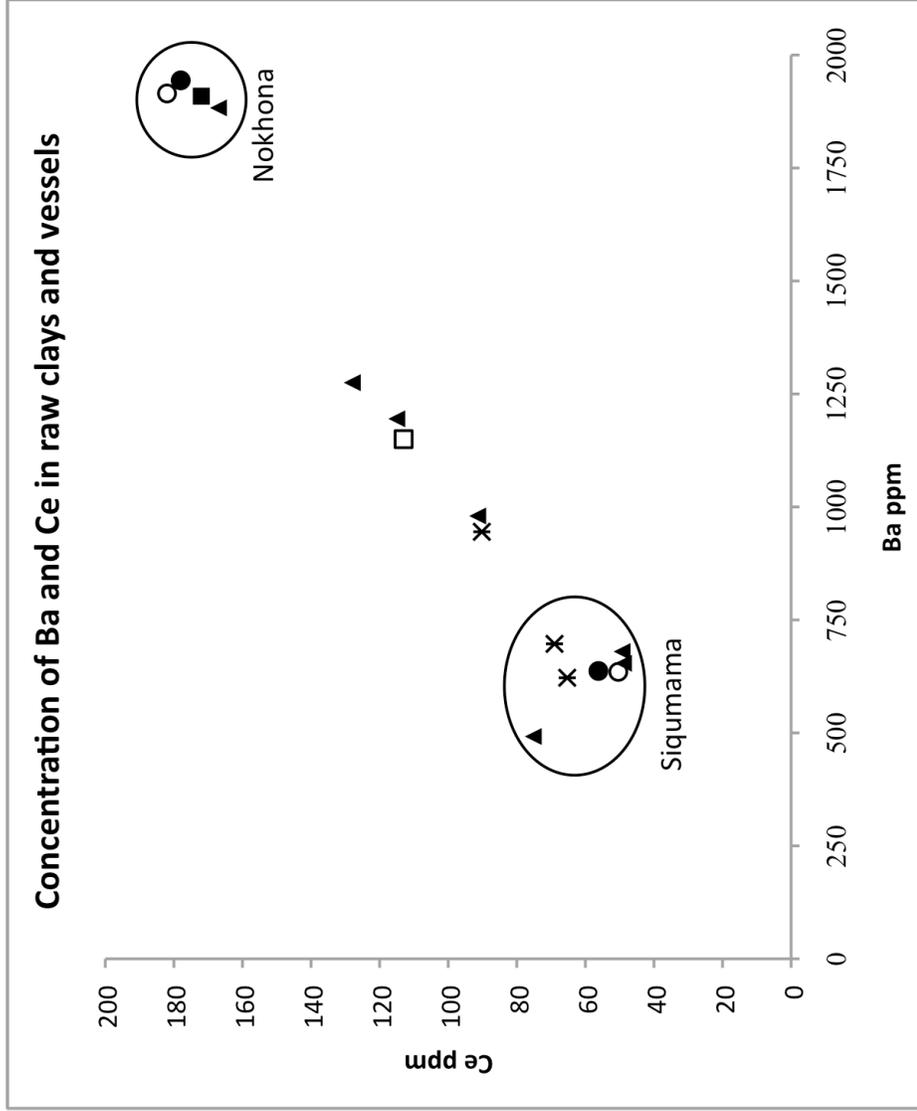
Figure 4.21 The concentration of Ba and Ce in raw and processed clays and vessels (see Table 4.7). Filled circles represent unprocessed clay, unfilled circles represent ground and sifted clay. Asterisks represent mixed processed clays. Filled squares represent nonplastics from a single source, unfilled squares represent mixed nonplastics, and triangles represent vessels.

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as mixed clays and vessels produced from these clays. Depending on the proportion of clay used in the mixture, mixed clays and vessels either have Ba and Ce concentrations similar to one of the raw clays, or intermediate between the two (Table 4.7, Figure 4.21). Turning back to Sample 16, the Zn content of this vessel is intermediate between clays from *Siqumama* and *Ntontonto*, which suggests that it was produced using a mixture of these clays.

Although potters generally use red clay from *Nokhona* to produce vessels, this sample represents a case in which black clay was mixed with red clay from *Ntontonto*, red clay being the larger proportion in the mixture. As with the other vessels, provenance could likely be determined for this sample at a regional level (it clearly is associated with a clay source in Nkandla). However, without ethnographic documentation of clay mixing, it would not be evident that this sample contains clay from other sources.

4.3 Summary

A combination of quantitative and qualitative methods was used to interpret the results of mineralogical and chemical analysis. The mineralogical data produced by XRD and SEM analyses were interpreted qualitatively, and compared with the results of chemical analysis. Chemical compositions were analyzed using multivariate statistics, including cluster analyses and principle components analysis (PCA). When the data are analyzed as a whole, samples fall into five categories. One category contains only samples from a single source (*Ndondondwane*), and the other four categories contain a combination of raw and processed clays, as well as finished vessels (Figure 4.9). The categories with the strongest division from the rest of the samples, as determined using PCA, are associated with clay sources *Siqumama*, *Nokhona* and *Ntontonto* (Figure 4.10).

After addressing the broad categories formed by the chemical data, results were considered in three stages. First, the composition of raw clay from each source was compared, highlighting similarities between *Siqumama* and river clay, and between *Ntontonto* and *Ndondondwane*. Samples were then compared according to processing stage. There appears to be no compositional difference between raw clays and those that have been ground and sieved, or between raw clays and nonplastics. However, mixed clays tend to form a separate compositional group, and it is only when they are analyzed using cluster analysis that similarities are revealed between mixed clays and the source that is most dominant in the mixture.

Finished vessels display the same tendencies as mixed clays, clustering according to the proportion of each raw clay present in the ceramic body. The degree to which vessels are associated with the major constituent clay varies, and seems to be related to the relative proportion of clay mixtures. XRD results do not reveal clear groups like the chemical data, but the minerals identified using XRD do conform to the regional geology of the study area. The mineralogical results of SEM analysis are also less useful for generating compositional categories than chemistry, but they help explain some of the values seen in the chemical data. The images of vessel samples produced by the SEM provide additional information about the character of finished vessels. Vessels can be described according to two main variables: the range of variation in grain sizes, as well as the shape and size of voids in the clay body.

In the following chapter, I will consider how these physical and chemical data may be used to infer the effects of the manufacturing behaviour of potters and how these behaviours impact the interpretation and identification of clay sources.

Chapter 5. Discussion

The results of chemical and mineral analyses can be used to determine how processing strategies affect the composition of finished vessels, and whether finished vessels can be associated with their constituent clay sources in spite of processing. For this thesis I set out to address two hypotheses. The first hypothesis is that there are observable differences between the mineral and chemical composition of raw clays and finished vessels. The second hypothesis is that these differences can be attributed to cultural factors. In this chapter I will discuss how the results of my research meet the predictions of these hypotheses, and how this affects our ability to determine the provenance of finished vessels. I will also evaluate the efficacy of the methods used to test these hypotheses and answer the research question.

5.1 Composition of Raw Clays and Finished Vessels

The first hypothesis I proposed to test in this thesis was that discernible compositional differences exist between raw clays and finished vessels. In order to test the hypotheses, I examined mineralogical and chemical differences between raw clays and finished vessels.

The mineralogical composition of clays and vessels does not vary enough to distinguish between individual sources, but it does help explain the chemical profiles of the clays. For example, clays from *Nokhona* have high levels of potassium oxide (K_2O), which is likely due to the presence of micas (muscovite and biotite) that were identified in vessels containing clay from *Nokhona* (Table 4.1), and also microcline, a potassium-

rich feldspar, that was detected in the XRD analysis of *Nokhona* clays (Table 4.3). Another unique chemical feature that can be explained using mineralogical data is the extremely high concentration of chromium (Cr) in Sample 16. Using SEM it was possible to detect the mineral chromite, which is likely the source of those high Cr levels (Table 4.1). Petrographic analysis makes it possible to understand the reason some elements are more concentrated in different clay sources. However, it is necessary to turn to chemical characterization data to clearly distinguish between individual sources and determine the provenance of vessels.

In order to examine whether there is variation between raw clays and finished vessels it was also necessary to determine whether clay sources could be distinguished based on their chemical composition. In contrast to the mineralogical data, the chemical data did distinguish the different sources. The component loadings in a principle component analysis reveals the elements that contribute the most to the variation in source compositions (Figure 4.12). High concentrations of sodium oxide (Na_2O) and strontium (Sr) are characteristic of clays from *Siqumama*. Clays from *Nokhona* can be distinguished by their levels of potassium oxide (K_2O), lanthanum (La), cerium (Ce) and thorium (Th), low concentrations of nickel (Ni) and chromium (Cr), and possibly by the presence of microcline (Table 4.3). Characteristic concentrations of Cr, zirconium (Zr) and Ni are observed in clays from *Ntontonto*. Finally, clays from *Ndondondwane* contain high concentrations of phosphorus pentoxide (P_2O_5) and zinc (Zn), and low levels of Na_2O.

Although the variation between sources is sufficient to distinguish clays from each source, the use of multiple statistical techniques is an important step in doing so.

When all samples are analyzed together using PCA, clays from *Ndondondwane* (Samples 21-23) are not clearly separated from the *Ntontonto* clays or from mixed clays and vessels (Figure 4.10). Cluster analysis reveals that although these samples share space in the PCA biplot, the clays from *Ndondondwane* have a very distinct composition (Figure 4.9).

When statistical analyses include all samples, some vessels are not compositionally distinct from raw clays, whereas others are. Samples 13 and 14 are consistently associated with clays from *Siqumama*, regardless of whether PCA or cluster analysis is applied. Similarly, Samples 15 and 25 are very strongly associated with clays from *Nokhona* in all cases, although the relationship is more pronounced with Sample 25. Where these samples are concerned, there is no significant difference in composition between raw clay and finished vessels. This group of vessels does not support the hypotheses, but their close association with raw clays can be attributed to the proportions of clays used in preparing clay bodies. This is an effect of potters' behaviour and will be taken up further below in the discussion of the second hypothesis tested in the thesis.

The strongest support for the first hypothesis comes from composition of four vessels that did not strongly cluster with *Nokhona* and *Siqumama* raw clays and mixed clays. These vessels display observable differences in composition to the raw clays from which they are manufactured. In the PCA biplot for all samples, vessel Samples 17, 18 and 19 are distributed in the centre of the plot, separate from each clay source, near the mixed clays (Samples 3-6, Figure 4.10). Sample 16 is separated further, positioned near raw and processed clays from *Ndondondwane*. Predictably, cluster analysis of all samples groups vessels 13 and 14 with clays from *Siqumama*, and vessels 15 and 25 with clays from *Nokhona* (Figure 4.9). Samples 17, 18 and 19 share a cluster with mixed clays, and

Sample 16 is grouped with clays from *Ntontonto*. When PCA is conducted using just vessel samples, only the locations of Samples 17, 18 and 19 change (Figure 4.15). These samples move from the centre of the plot to join the group formed by Samples 15 and 25. This suggests that the composition of these pots is similar, but that the composition of Samples 17, 18 and 19 is sufficiently different from that of pure clays from *Nokhona* to separate them statistically. These samples demonstrate that discernible compositional differences exist between raw clays and finished vessels. In order to assess the second hypothesis, it is necessary to discuss how these compositional differences are introduced.

5.2 Sources of Compositional Variation

Compositional differences exist between raw clays and some finished vessels. The source of these differences can be determined by comparing the composition of clays at each stage in the processing sequence with raw clays to discover when changes arise. This analysis demonstrated that variation is introduced during two manufacturing activities: clay acquisition and clay processing

5.2.1 Variation Attributable to Clay Acquisition

In the first stage of processing, raw clays are ground and sieved to remove nonplastic inclusions. Statistical analysis of ground and sifted clays, as well as the nonplastics removed with a sieve, reveal no significant compositional changes as a result. Sifted clays and nonplastics cluster very strongly with the raw clays that have not been subjected to any processing (Figures 4.9 and 4.10). The lone exception to this rule seems to be Sample 20, sifted clay from *Ntontonto*.

As I have previously discussed (in Section 4.4), Sample 20 was collected directly from potters, and a duplicate sample (Sample 11) was manufactured in the lab, in order to produce nonplastics for analysis. Sample 20 appears to be similar to clays from *Ndondondwane* according to the PCA biplot (Figure 4.10), and cluster analysis groups this sample with mixed clays from *Siqumama* and *Nokhona* (Figure 4.14). The deviation in composition may be due to either natural or behavioural factors. If Sample 20 was collected from a different section of the extraction site than Sample 11, it could represent an extreme in the compositional variation naturally present at *Ntontonto*. However, given the accuracy with which each clay source in this study forms a cluster, it seems unlikely that natural variability could be responsible for the composition of Sample 20. Behavioural factors related to resource procurement are more likely to account for the discrepancy in composition between Sample 20 and other clays from the same source. Heavy rains cause the topsoil at this particular extraction site to slump downward, covering the clay strata below. It is common practice for potters to send children to collect clay, and they may be inexperienced at distinguishing between soil and clay in the strata at an extraction site. If the slumped soil was not completely cleared from the extraction site before clay was collected, the composition of the red clay sample would be contaminated with topsoil. The chemical differences between Samples 11 and 20 are likely due to the effects of this clay acquisition behaviour.

5.2.2 Variation Attributable to Clay Processing

The variation in finished vessels that can be attributable to clay processing is discernable in the both the physical structure of the fabric and in the chemical composition of vessels.

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The size and shape of voids and the size of mineral inclusions show the effects of processing on the physical structure of vessels. The shape and orientation of the voids in each sample are most likely related to the direction in which the vessel was cut during sampling, either parallel or perpendicular to the coils of the vessel wall. Those that show strong orientation appear to have been cut perpendicular to a coil, whereas more random orientation results from a sample being taken parallel to a coil.

It is possible to divide the vessel samples into three structural groups, defined by the range of size variation observed for mineral inclusions (Table 4.2). These variations may be related to processing behaviour, particularly grinding and sieving. The raw clay used to produce the vessel collected in 2002 (Sample 25) was not sieved, and the range of variation observed in the size of its inclusions is very large. Two other vessels (Samples 14 and 17) display similarly large ranges of inclusion size (Table 4.2). One of those vessels (Sample 17) was produced by a novice potter, and the relative lack of experience of that individual may explain why grains were not ground to a more homogenous consistency. However, there is no reason to believe that the potter who manufactured the final vessel (Sample 14) would have a similar lack of skill. The vessels with very homogenous grain sizes (Samples 15 and 19, Group 1 in Table 4.2) were both manufactured by senior potters. It is possible that their years of experience processing clay results in more consistent grain sizes. Although it is impossible to conclude that there is a clear relationship between processing behaviour and grain size due to the relatively small number of vessel samples in this study, it is a topic that warrants further research.

Chemical data provides further insights into the observable effects of processing behaviour on composition. In nearly all case, potters interviewed in Nkandla reported mixing red and black clays in equal proportions, and that that they typically combine clays from *Siqumama* and *Nokhona*. The combination of clays from the two sources significantly alters their composition, differentiating them from both raw clay sources. Samples 3, 6 and 26 are mixed clays (Sample 26, collected in 2002, was recorded as pure black clay, but is in fact mixed clay), and Samples 4 and 5 are mixed nonplastics. Analysis of principle components shows Sample 26 to be separated from other samples, between clays from *Siqumama* and *Nokhona*, with the other mixed samples spread out in the centre of the biplot (Figure 4.10). Cluster analysis groups Sample 26 with clays from *Nokhona* and two vessels, and the remaining mixed samples are grouped with three vessels and Sample 20 (Figure 4.9). These mixed samples are, at the next level of agglomeration, grouped with clays and from *Siqumama*. The same pattern is produced when raw and mixed clay samples are analyzed in the absence of finished vessels (Figure 4.14).

This effect is likely produced by variation in the proportion of raw clays added to the mixture. Sample 26 appears to be compositionally distinct in the PCA biplot, but cluster analysis reveals that its composition is closely related to that of clays from *Nokhona*. Clay from this source constitutes part of the mixture in Sample 26, and it would seem to be the dominant component, as the mixed clay more closely resembles this source than either black clay source. Similarly, Samples 3 through 6 are grouped with clays from *Siqumama*, albeit at the second level of agglomeration. Again, this suggests

that they more closely conform to the average chemical profile of that source, which probably constitutes the larger portion of the mixture.

Knowing the effect that clay mixing has on vessel composition also helps explain what initially appear as anomalous samples during analysis. Vessel Sample 16 was originally documented as being composed of a mixture of black clay from *Siqumama* and the red clay from *Ntontonto*. Cluster analysis revealed that Sample 16 shares compositional characteristics with clays from *Ntontonto*, and the relationship was significant enough to group them together. However, based upon a comparison of the concentrations of Na_2O and Zn in the samples (Figure 4.20), it is more likely that Sample 16 represents a vessel in which black clay from *Siqumama* was mixed with red clay from *Ntontonto*, not red clay from *Nokhona* as was previously assumed. Likewise, 17 through 19 appear to contain an even mixture of clay from each source, based on their positions in the cluster analysis dendrogram and the PCA biplot (Figures 4.9 and 4.10). However, when PCA is conducted for vessel samples alone it becomes clear that these vessels are very similar in composition to Samples 15 and 25, which are strongly associated with clays from *Nokhona* (Figure 4.15). It can therefore be concluded that vessel Samples 17 through 19 contain a significant amount of clay from that source.

5.2.3 Variation Attributable to Firing

The final stage in ceramic production, firing, does not seem to significantly alter the composition of clays. The results of both PCA and cluster analysis show that some fired vessels are very strongly associated with raw clay sources. As discussed above, vessel Samples 13 and 14 are consistently grouped with clay from *Siqumama*, and Samples 15 and 25 are grouped with clay from *Nokhona*. However, it is known from

ethnographic observation that all of these samples contain clay from both sources. The same forces that affect the composition of mixed clays are likely at work here. The mixture of red and black clay represented in these samples seems to be uneven, with the major component exerting more influence on chemical composition.

5.2.4 Summary

The composition of ceramic materials can be affected by geochemical factors associated with clay sources, or by cultural factors associated with ceramic production. If geochemical factors are the only source of variation, the composition of finished vessels would not exhibit significant differences from the composition of raw clays. However, it is clear from the foregoing discussion that cultural factors have the potential to alter ceramic composition. Of all the stages involved in clay processing and ceramic manufacture, it appears that the mixing of clays from different sources is the only one that significantly alters clay composition. When clays are mixed, the effect on composition is consistent in that the proportion of clays will determine the source to which finished vessels are most similar. Although the compositional changes produced by processing strategies are predictable, it is also necessary to discuss whether it is possible to determine the provenance of vessels despite this effect.

5.3 Processing Behaviour and Provenance

The results of statistical analyses show that some vessels reflect their provenance more clearly than others. If the proportion of one clay in a mixture is quite high, finished vessels will be strongly associated with that clay source. When the proportions of both clays are more even, the provenance of vessels is somewhat obscured, as with vessel

Samples 17 through 19. However, a combination of cluster analysis and PCA of vessel samples correctly associates them with the source of their main constituent material. These results suggest that it is possible to correctly determine the provenance of ceramic vessels in spite of the effects of processing – but only to a degree.

5.3.1 Can Tempered Vessels be Provenanced?

In their analysis of the effects of production behaviour on provenance, Arnold and colleagues (1991:75) concluded that tempered vessels cannot be related to single, specific sources of raw material, since they reflect the weighted proportions of clay and temper in the recipe. Were this the case, then using another clay as temper could be expected to create a clay of intermediate composition, not strongly associated to either source. This is also the compositional profile that Bishop and colleagues (1982) anticipate when a compounding resource procurement strategy is employed, such as that used by Zulu potters. My results demonstrate that this effect can be observed in tempered vessels – mixing clays *may* produce an intermediate composition – but this is not always the case. If one clay is represented in a higher proportion, the compositional profile of the finished vessel will be similar to a single source, not an intermediate between two sources.

To elaborate, it may be evident that vessels contain clay from more than one source because of their relationship to other clays and vessels, shown by PCA or cluster analysis. Knowing that mixing has occurred does not necessarily make it possible to determine what combination of clays are represented in a vessel. For example, in this study vessel samples grouped most strongly with one or the other of their source materials. If I was not already aware of which sources were used to produce vessels, each sample could only be associated with one source and the reality that vessels were

comprised of clays from two sources would not be revealed using these statistical methods. However, I was also able to identify mixtures that were not reported by potters (Samples 16, 25 and 26) because in all cases the *unreported* clay was dominant in the mixture. If the *reported* clay had been dominant in these samples, no further investigation would have been warranted, and the ethnographically reported composition would have been accepted. The best example of this effect is Sample 16.

During analysis, it was assumed that the vessel represented by Sample 16 was manufactured using the same combination of clays contained in the other vessel samples. Statistical analyses revealed that this is not the case, and that Sample 16 contains a different red clay than the other vessels. It was only possible to reach this conclusion because the red clay is represented in a higher proportion than the black, causing Sample 16 to group with clays from *Ntontonto*. If clay from *Siqumama* had been the major component, Sample 16 would likely have grouped with that source, and it would not have been evident that this particular pot contains a different red clay than the rest.

When it is known or discovered that clays have been mixed, the constituent clays may be identified by examining ratios of elements that exhibit a high standard deviation, which makes the relative concentration of these elements characteristic of particular sources. The principal of mass conservation (discussed in Section 4.5) can be used to infer which raw clays are present in a mixture. For example, if a mixture contains a high concentration of Ni, and only one raw clay has high levels of Ni, then that clay *must* be a constituent of the mixture. Applying the principle of mass conservation in this case aids in identifying clays that are present in a mixture.

5.3.2 Sampling and Research Design

The effects of mixing render provenance studies of archaeological material more difficult. When processing behaviour is unknown, the interpretation of statistical analyses can be problematic. Cluster analysis has proven to be very useful for discerning compositional groups. However, it is in the nature of this method to detect clusters in any set of data, regardless of whether those clusters represent meaningful compositional groups, and it is then a matter of subjective interpretation as to which levels of clustering are relevant (i.e. accurately represent relationships between compositional data and human behaviour) (Baxter 1994:155). In this study, clusters could be assessed using prior knowledge about how clays were mixed. Most provenance studies that involve archaeological ceramics do not have that luxury. It is therefore important that studies like this one are undertaken to interpret statistical groups and infer provenance from compositional data when using ceramics from archaeological contexts. It is best if such studies are conducted on a case by case basis using local and regional comparative data.

This study shows that a range of compositional variation can exist between sources in a local area. In an archaeological context, this level of compositional variation can make it difficult to distinguish between local and non-local vessels (Bishop, et al. 1982). If there is a high degree of geological variation within a study area, the composition at different extraction sites needs to be understood for provenance research to be successful. Once again, vessel Sample 16 serves as a good indication of this requirement. Almost all of the vessel samples included in this data set could be grouped within two clusters when PCA was conducted for vessels alone (Figure 4.15). Sample 16 is an outlier, and does not fit into either of the clusters. This vessel would appear to be

non-local if the compositional range represented in local clays was not known. When archaeological provenance studies neglect to include local clay samples, they run the risk of mistaking outliers for imports. However, if there is very little geological variation in a study area, local clays are less likely to produce extreme outliers like Sample 16, and provenance research may not be impacted so drastically.

5.3.3 The Effects of Clay Mixing

The most important implication of these analyses is that the ratio of clays combined during processing can have a significant effect on composition. Jacobson (2005:37) argues that the consistency of clay ratios has implications for the success of provenance research. If a variety of ratios are used, they will produce vessels with different compositions, making it more difficult to determine which vessels were manufactured locally. The results of this study demonstrate that potters in Nkandla are *not* consistent in the ratio of clays they combine. Although this inconsistency did result in different compositions, it did not preclude sourcing.

Clays from *Siqumama* and *Nokhona* mixed in different ratios produce vessels that fall into three different compositional groups (although further analysis demonstrates that each group can ultimately be associated with one or both of the original sources). Jacobson (2005) recognizes the potential that multiple chemical groups may be observed due to inconsistent mixing ratios. He suggests that if most of the vessels from a site fall into a few chemical groups, it can be assumed that all of the groups are local. Vessels that do not fall into one of the defined groups are more likely to be non-local. However, using this approach without understanding local geochemical variation would still lead to the conclusion that outliers like Sample 16 are non-local. The best way to compensate for

local variation is to include clay samples from the study area, in the hope that they will accurately represent the full range of compositional groups that might be encountered.

Even when compositional data accurately distinguish between local and non-local clays, it is not a simple matter to explain the presence of non-local material. It is common practice in provenance research to correlate non-local composition with the trade or transport of finished vessels. In reality, this conclusion is not straightforward. There are precedents for the movement of raw clays and temper over large distances (e.g. Wilmsen, et al. 2009), and it is far easier to carry clay than it is to transport finished vessels and their contents. If the movement of pottery is to be inferred from compositional data, it should be corroborated using other evidence, such as stylistic data.

5.3.4 Compositional Data and Technological Choice

Compositional studies like this one are useful beyond provenance identification. Geochemical data can reflect other aspects of cultural behaviour. In Nkandla, as in many places where pottery production remains part of the local economy, groups of potters tend to work together, sharing resources and technological knowledge. These communities of potters can be identified based on evidence of similar technological choices. My research suggests that compositional data may be used to reconstruct technological choices related to resource procurement and processing behaviours. The results of this research show that tempering (by mixing clays) is the only processing stage that has a significant effect on composition, although its effect is not always pronounced. Where the effect is discernible across all local pottery, it provides evidence that potters are making similar technological choices because they are part of the same learning (or social interaction) network, which will be distinct from other networks.

Resource procurement patterns can also indicate that potters are part of the same social networks, which define a larger community of potters. Clay sources are generally identified during daily activities, and their locations are shared amongst a community (Arnold 2005; Gosselain and Livingstone Smith 2005). Ceramics that are produced by different potters using the same resources help define such a community. When resource procurement patterns can be inferred from compositional data, they also provide information about the size of resource areas exploited by potters, and the distance potters are willing to travel to collect clay.

Communities of potters form the social network through which knowledge is transmitted to the next generation of artisans. We have seen that production behaviour is primarily responsible for compositional variation between clay sources and finished vessels, and that behaviour is learned. Ingold (2000) has argued that performance is the primary source of variation in material culture. In the context of ceramic provenance this implies that the performance (behaviour) of potters is responsible for compositional variation. This argument is consistent with the results of my research. The functional limitations that affect ceramic composition are very broad, and it is possible to successfully produce a ceramic vessel using a wide range of manufacturing techniques. However, potters beliefs about functional limits are fairly constrained; potters tend to believe that the *only* way to produce a useable vessel is the way they were taught. Therefore, behaviour, constrained by the social network, significantly affects the composition of ceramic vessels.

5.4 Evaluation of Methods

Following the example of other provenance studies, I used multiple characterization techniques to assess how composition is affected by different stages in a ceramic production sequence. The mineral constituents of clay and vessel samples were identified using SEM and XRD, and the physical structure of vessels was also analyzed by SEM. Chemical characterization was undertaken using ICP-MS, to quantify the concentration of major and trace elements in clay and vessel samples. Each of these methods will be discussed with regard to their contribution to understanding the compositional changes associated with clay processing and ceramic production.

The identification of mineral inclusions using SEM was quite effective. Obtaining a mineralogical profile for vessel samples alone could not be used to determine their provenance. However, the mineralogy of samples is consistent with the surficial geology of the study area, and these data could be very useful when comparing vessels from distinct geological regions. Comparison of the physical structure of vessels revealed that processing behaviour may be reflected in structural variations. However, understanding the nature of this relationship is a topic for future research.

The data produced using XRD were less useful for defining compositional groups and determining provenance, in part because of the inherent difficulty of analysing the complex mineralogy of clay samples. Only major constituents (>2%) can be identified using XRD, which restricts the amount of compositional data that can be collected using this technique (Bishop, et al. 1982:284). Even major constituents can be obscured by the complex mixture of minerals that are present in clay, or by individual minerals that occur in high concentrations (such as quartz). Both of these problems were encountered in my

analyses. The compositional spectra produced by mixed clays were too convoluted to allow individual minerals to be identified. In some samples, the strong peak produced by quartz diminished the peaks of other mineral constituents. Comparing the different analytical techniques employed in this research, I would conclude that XRD was the least useful. Steps could be taken to increase its efficacy, for instance removing most of the quartz from clay samples, and this might increase the accuracy with which clay minerals can be identified.

Chemical analysis is now a standard analytical approach in provenance research. In particular, trace elements profiles are often used to determine provenance because it is assumed that trace elements are unlikely to have been added as temper (Pollard and Heron 2008:101). This is not the case when clays are combined, since mixing effectively adds trace elements as part of the tempering process. However, the alteration of trace element profiles during processing is not a liability but an asset in this research, as compositional changes provide evidence for processing behaviour, and still allow vessels to be associated with individual clay sources. It is becoming clearer how strongly behavioural factors contribute to the compositional variation of ceramics.

Due to its sensitivity to changes in composition, ICP-MS was invaluable for determining how processing alters clay. The quantitative data produced by ICP-MS are well suited to statistical analysis, making it relatively straightforward to identify compositional groups within the data.

Although mineralogical data alone are rarely sufficient for determining provenance, they can be compared with chemical data to identify the minerals responsible for the concentration of different elements in individual samples. While chemical analysis

is the more powerful method for distinguishing between clays and detecting the effects of processing, it should be used in combination with petrography to develop a broad understanding of composition. The relative utility of these methods is also related to the scale of analysis. On a larger regional scale, mineralogical differences may be sufficient to begin to address provenance. Small-scale studies like this one rely more heavily on trace element concentrations to differentiate between individual clay sources.

Each of the statistical methods used in this study imparts valuable information about compositional groups, and they are highly effective when used in combination. The output of PCA and cluster analyses identifies distinct compositional groups, and the results obtained using each method can be compared to assess their validity. Cluster analysis also provides information about the relationships between groups, specifically how compositionally similar they are. Finally, the analysis of pairs of element ratios provides a means of identifying both constituent clays in a mixture.

5.5 Summary

The implications of my research for provenance studies are generally optimistic. Having analyzed the effects of behaviour on ceramic composition, I can conclude that although processing behaviours (specifically, mixing or tempering) do alter clay composition, it is still possible to associate finished vessels with individual clay sources. However, my results also demonstrate that the ratio of clays in a mixture has an appreciable effect when attempting to determine provenance. The clay that is represented in a larger proportion has the most significant effect on the composition of a finished vessel, and this will vary between batches of clay. When ceramic vessels are produced from a mixture of clays, it does not affect our ability to distinguish between local and

non-local clays. It *does* limit the accuracy with which the constituent clays can be determined: vessels will tend to be associated with a single, dominant source. However, detailed examination of element ratios can identify both constituent clays. If the aim of research is only to determine provenance, the identification of one constituent clay source would likely be sufficient, because it clearly associates a vessel to a local area. However, if the aim is to reconstruct processing behaviour, the inconsistency of ratios of mixed clays is very problematic.

In archaeological research provenance is usually defined at a regional scale, because the concept of what constitutes a "source" is so problematic (Arnold, et al. 1991; Jacobson 2005), and because geochemical variation is almost guaranteed to exist between different regions (Jacobson 2005). The results of this research show that sufficient variation is present at a very small scale to distinguish between clay sources, but conducting provenance research at a regional scale increases the confidence with which local and non-local vessels can be distinguished. However, even at a regional scale it would be advisable to include raw clay samples from a variety of sources, to account for local geochemical variation and to avoid misinterpreting vessels that belong to compositional extremes.

Chapter 6. Conclusions

Ceramic provenance studies attempt to associate finished vessels with raw clay sources in order to distinguish between local and non-local vessels, which allow researchers to make inferences about exchange and mobility patterns. However, in addition to natural factors related to clay composition, behavioural factors have the potential to influence the composition of finished vessels. These behavioural factors include resource procurement, clay processing, and firing. Variation can be addressed in terms of both mineralogical and chemical composition, as determined using a combination of petrographic and chemical characterization techniques.

Previous research in southern Africa has typically relied on the comparison of archaeological and modern vessels, without the use of raw clays to represent geochemical variation in a study area. This approach is usually taken in order to avoid addressing how behavioural factors affect clay composition. However, this approach also introduces new problems, because it is not able to account for the full range of variability that may be present in local clays. To facilitate comparisons between finished vessels and raw clay sources, it is first necessary to assess whether significant compositional differences are introduced during manufacture.

In this study I set out to determine whether the composition of clay is altered during the ceramic production sequence, and, if so, whether it is still possible to associate finished vessels with raw clay sources. To answer this question, I tested two hypotheses. First, that there are observable compositional differences between raw clays and finished vessels, and second, that these differences can be attributed to cultural factors. I used

mineralogical and chemical characterization techniques to analyze samples from each stage of an ethnographically documented ceramic production sequence amongst Zulu potters in KwaZulu-Natal, South Africa. Individual stages in the production sequence that have the potential to alter ceramic composition include the removal of nonplastic inclusions, the addition of temper, and the firing of finished vessels. Although some of the effects of tempering have been addressed in previous research (Arnold 2005; Neff, et al. 1988), Zulu potters in this area mix clays from different local sources to produce clays deemed appropriate for potting, which will introduce problems into any attempt to relate finished vessels to clay sources.

A combination of XRD and SEM analyses were used to determine the mineralogical composition of samples, and ICP-MS was used to measure the major and trace elements present in each sample. Compositional groups were distinguished in the chemical data using multivariate statistical methods, including cluster analysis and principle component analysis, and element ratios were also used to identify constituent clays. The composition of clays was compared at each stage of the production sequence, to determine whether processing behaviour is a factor that causes variation. The results of mineralogical analyses were compared with the chemical data to look for additional evidence of changes in composition.

Statistical analysis revealed five main compositional categories in the chemical data. These categories effectively distinguish between raw clays associated with different sources, and between raw clays and mixed clays. Finished vessels were found to differ from raw clays to varying degrees, determined by the relative proportion of each constituent clay in the ceramic body.

In regard to my first hypothesis, that significant compositional differences exist between raw clays and finished vessels, the results of this research indicate that this is true in some cases, but not in *all* cases. When the clay body contains a significantly large amount of clay from one source, the finished vessel does not appear to be compositionally distinct from the dominant clay source in the mixture (for example, vessel Samples 13 and 14 group strongly with clays from *Siqumama*). If a more equal ratio of clays is used, an intermediate composition will result, and the finished vessel will have a different composition than either source (as with vessel Samples 17-19). The second hypothesis, that this compositional variation is introduced by production behaviour, is confirmed by the strong association between a particular stage in the production sequence – tempering, accomplished by mixing clays – with changes in ceramic composition.

In response to the research question – whether it is possible to associate finished vessels with clay sources despite the effects of processing – the results of this study demonstrate that when clays are mixed it is still possible to determine at least *one* source used to manufacture a vessel, and sometimes both sources. In other words, it is still possible to determine the provenance of the vessel, since it can be associated with a local source.

The results of this research have implications for ceramic provenance studies, and for our ability to reconstruct different aspects of ceramic production in archaeological contexts. I have demonstrated that it is possible to determine the provenance of ceramic vessels even when their composition has been altered due to processing. In doing so, I discussed the importance of including raw clay samples from the study area to establish

the range of geochemical variation observed locally. It is hoped that, using the results of this research, future provenance studies will produce more sophisticated interpretations that account for the processing techniques employed by potters.

It may also be possible to reconstruct those processing techniques by building on the results of this research. When the processing sequence is unknown, but the ratio of clays in a vessel produces an intermediate composition, it would be possible to use that information to conclude that potters are mixing clays. However, the mixing of clays does not always result in a composition that can readily be identified as intermediate. Further research is required to determine whether it is possible to identify the ratios of different clays present in a vessel, rather than simply associating the vessel with a single source.

This research also has applications using ceramic composition to infer cultural behaviour associated with ceramic production. First, by comparing archaeological vessels with local clays it may be possible to define the boundaries of resource areas exploited by potters. Second, by determining the extent to which technical knowledge is shared amongst potters, evidence may be found for the existence of communities of potters who work together, sharing resources and techniques. Evidence for this kind of cooperation would include multiple potters exploiting the same clay sources, since the sharing of information about resources implies cooperation.

The results of this research raise more questions, in addition to those already discussed, which warrant further investigation. Petrographic analysis of vessel samples revealed a possible correlation between forming techniques and the internal structure of the ceramic body. This relationship needs to be examined in more detail to determine

whether the correlation is predictable, in which case it may be used to reconstruct production techniques from recovered vessels.

Most importantly, the conclusions I have drawn here should be tested in an archaeological context. A provenance study that uses archaeological material, and incorporates a survey of local clay resources, will help assess whether understanding local geochemical variability results in a more robust interpretation of compositional data.

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Report: A11-4845

Analyte Symbol	SiO2	Al2O3	Fe2O3(T)	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	LOI	Total
Unit Symbol	%	%	%	%	%	%	%	%	%	%	%	%
Detection Limit	0.01	0.01	0.01	0.001	0.01	0.01	0.01	0.01	0.001	0.01		0.01
1	60.83	15.53	6.56	0.083	1.98	4.58	3.23	1.09	0.551	< 0.01	6.15	100.6
2	60.26	15.48	6.23	0.076	1.92	4.5	3.28	1.07	0.529	0.02	6	99.35
3	59.07	15.76	8.03	0.098	2.41	4.04	2.84	1.17	0.864	0.05	6.48	100.8
4	60.47	15.68	7.45	0.092	2.32	4.08	2.97	1.09	0.817	0.02	5.76	100.8
5	55.53	15.13	7.52	0.109	2.25	6.25	2.48	1.6	0.812	0.14	8.02	99.83
6	59.41	16.56	7.01	0.095	2.06	4.52	3.04	1.49	0.724	0.09	5.79	100.8
7	56.68	18.47	7.64	0.111	1.42	3.86	2.29	3.01	0.606	0.28	5.8	100.2
8	57.6	17.61	7.37	0.117	1.42	4.03	2.22	3.02	0.59	0.29	5.41	99.7
9	56.61	18.14	7.17	0.115	1.31	3.8	2.37	3.01	0.568	0.27	5.07	98.44
10	54.95	15.49	10.06	0.113	3.09	2.96	2.35	1.16	1.331	0.06	7.25	98.81
11	55.71	15.68	10.44	0.114	3.01	2.81	2.3	1.18	1.302	0.11	7.47	100.1
12	55.62	15.61	10.59	0.149	3.03	2.78	2.4	1.17	1.314	0.06	7.37	100.1
13	62.75	16.69	6.26	0.081	2.16	4.97	3.65	1.11	0.548	0.02	1.44	99.68
14	62.83	16.96	5.63	0.076	1.91	5.04	3.7	1.13	0.502	0.02	1.49	99.29
15	58.55	18.32	7.9	0.119	1.67	3.99	2.38	2.79	0.702	0.24	2.82	99.49
16	57.24	14.91	9.64	0.124	5.76	4.05	2.17	0.87	1.016	0.05	2.45	98.28
17	59.49	16.72	7.94	0.109	2.36	4.72	2.98	1.89	0.913	0.17	2.72	100
18	57.34	16.94	8.57	0.12	2.72	4.36	2.68	1.99	0.952	0.17	2.55	98.4
19	60.4	16.48	7.16	0.1	2.11	4.68	3.14	1.55	0.73	0.11	2.74	99.19
20	58.4	16.23	8.54	0.104	2.53	3.56	2.69	1.46	1.003	0.09	6.17	100.8
21	57.76	11.11	9.84	0.24	2.06	4.89	1.09	1.02	1.861	0.67	8.12	98.65
22	56.66	11.56	9.3	0.216	2.07	4.97	1.24	1.13	1.892	0.73	9.41	99.18
23	55.33	11.86	12.33	0.316	2.44	6.03	0.9	0.88	1.846	0.51	6.26	98.71
24	55.22	15.54	7.91	0.074	3.4	3.86	2.56	1.33	0.718	0.1	9.23	99.93
45	58.44	18.51	7.8	0.125	1.81	3.89	2.52	3.07	0.621	0.25	3.02	100.1
46	57.32	17.27	6.94	0.094	1.77	4	2.48	2.55	0.559	0.2	5.59	98.77

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Analyte Symbol	Sc	Be	V	Ba	Sr	Y	Zr	Cr	Co	Ni	Cu	Zn	Ga
Unit Symbol	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Detection Limit	1	1	5	3	2	2	4	20	1	20	10	30	1
1	20	2	120	637	616	14	160	80	21	40	40	60	15
2	19	1	117	635	631	12	106	80	18	40	40	60	15
3	20	2	153	697	518	16	150	170	25	70	50	70	16
4	21	2	157	622	528	15	147	180	22	80	50	80	17
5	19	2	149	1150	597	19	166	100	20	50	50	70	16
6	20	2	145	945	631	17	150	100	19	40	40	70	16
7	17	3	151	1944	556	20	201	40	19	20	40	50	16
8	16	3	148	1909	543	24	200	30	21	20	50	50	17
9	15	3	143	1915	544	22	209	40	22	< 20	40	50	16
10	21	2	192	606	339	22	219	290	31	150	60	90	20
11	22	2	196	666	328	22	211	290	32	150	60	90	18
12	22	2	202	659	334	21	216	290	46	140	60	90	19
13	20	1	136	654	677	14	117	120	16	60	40	60	15
14	20	1	126	680	694	15	112	90	14	40	30	50	16
15	18	3	159	1883	554	22	206	80	23	40	50	60	17
16	27	2	176	492	374	17	177	790	44	230	50	70	18
17	20	2	158	1195	620	22	205	110	20	50	50	80	17
18	21	2	166	1275	596	22	215	190	26	70	50	80	18
19	20	2	145	980	636	19	161	110	20	50	40	70	16
20	20	2	167	849	459	20	189	210	28	90	50	70	17
21	18	1	177	485	357	20	162	220	24	40	40	110	15
22	17	2	170	542	383	18	168	220	24	40	40	120	15
23	20	1	233	387	489	21	155	190	28	40	40	110	17
24	19	1	180	884	586	14	120	110	27	50	70	70	17
45	17	3	158	1870	599	23	215	50	22	30	50	60	16
46	16	2	141	1686	586	20	173	50	17	30	40	50	15

Final Report
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Analyte Symbol	Ge	As	Rb	Nb	Mo	Ag	In	Sn	Sb	Cs	La	Ce	Pr
Unit Symbol	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Detection Limit	1	5	2	1	2	0.5	0.2	1	0.5	0.5	0.1	0.1	0.05
1	2	< 5	37	9	< 2	< 0.5	< 0.2	2	0.6	1.4	25.1	56.2	5.71
2	1	< 5	34	8	< 2	< 0.5	< 0.2	1	< 0.5	1.3	23.3	50.4	5.2
3	1	< 5	45	15	< 2	< 0.5	< 0.2	2	0.7	2.3	33.1	69	7.2
4	2	< 5	42	16	2	< 0.5	< 0.2	2	0.7	2.2	30.5	65.3	6.79
5	2	< 5	61	17	< 2	< 0.5	< 0.2	2	0.8	2.4	57.4	113	11.7
6	2	< 5	53	14	< 2	< 0.5	< 0.2	2	0.7	2	44.7	90.2	9.39
7	2	< 5	109	11	< 2	< 0.5	< 0.2	2	0.8	3.1	93.7	178	18
8	2	< 5	111	11	< 2	< 0.5	< 0.2	3	< 0.5	2.9	89.9	172	18.2
9	2	< 5	110	10	< 2	< 0.5	< 0.2	2	0.9	3.1	93.5	182	18.2
10	2	< 5	54	27	4	< 0.5	< 0.2	3	0.8	3.7	38.8	78.5	8.67
11	2	< 5	54	26	4	< 0.5	< 0.2	3	0.8	3.7	38.5	78.7	8.53
12	2	< 5	53	26	4	< 0.5	< 0.2	3	0.7	3.7	39.6	102	8.88
13	1	< 5	35	9	< 2	< 0.5	< 0.2	2	0.7	1.5	22.6	48.9	5.07
14	2	< 5	35	8	< 2	< 0.5	< 0.2	1	0.8	1.4	22.3	49.3	5.1
15	2	< 5	103	13	< 2	< 0.5	< 0.2	2	0.7	3.2	86.9	167	17.2
16	2	< 5	39	20	3	< 0.5	< 0.2	2	0.9	3.3	38.2	75.2	8.13
17	2	< 5	64	19	< 2	< 0.5	< 0.2	2	0.6	2.6	61.7	115	12.5
18	2	< 5	75	21	< 2	< 0.5	< 0.2	2	0.8	3	68	128	14.2
19	2	< 5	54	14	< 2	< 0.5	< 0.2	2	0.8	2.1	46.3	91.4	9.77
20	2	< 5	55	19	3	< 0.5	< 0.2	2	0.6	2.8	42.6	88.8	9.06
21	2	< 5	32	27	< 2	< 0.5	< 0.2	2	< 0.5	1.2	22.1	49.4	5.21
22	2	< 5	37	28	< 2	< 0.5	< 0.2	2	0.5	1.4	23.2	49.3	5.45
23	3	< 5	27	27	< 2	< 0.5	< 0.2	3	0.8	0.9	20.9	49.1	5.27
24	1	< 5	48	9	< 2	< 0.5	< 0.2	1	0.5	1.8	39	75.2	8.65
45	2	< 5	108	11	< 2	< 0.5	< 0.2	2	0.8	3.3	92.4	172	18
46	2	< 5	86	9	< 2	< 0.5	< 0.2	2	0.8	2.6	72	136	14.3

Analyte Symbol	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta
Unit Symbol	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Detection Limit	0.1	0.1	0.05	0.1	0.1	0.1	0.1	0.1	0.05	0.1	0.04	0.2	0.1
1	22.1	4.4	1.21	3.5	0.5	2.9	0.6	1.6	0.25	1.6	0.26	2.7	0.6
2	20.2	3.9	1.17	3.2	0.5	2.7	0.5	1.6	0.23	1.5	0.24	2.5	0.5
3	27.4	5.4	1.45	4.1	0.6	3.4	0.7	1.9	0.28	1.9	0.33	3.6	1.1
4	25.8	5.1	1.49	4.1	0.6	3.6	0.7	2	0.3	2.1	0.34	3.7	1.2
5	42.8	7.7	2.11	5.9	0.8	4.3	0.8	2.3	0.33	2.1	0.36	4.1	1.2
6	34.7	6.1	1.68	4.8	0.7	3.6	0.7	2	0.29	2	0.33	3.6	1
7	64.2	10.6	2.61	7.3	0.9	4.4	0.8	2.2	0.33	2.2	0.37	4.4	0.6
8	64.3	10.6	2.43	7.1	0.9	4.6	0.8	2.3	0.33	2.2	0.35	4.8	0.6
9	63.9	10.7	2.55	6.9	0.9	4.4	0.8	2.3	0.32	2	0.31	4.9	0.6
10	33	6.2	1.72	5.3	0.8	4.6	0.9	2.3	0.33	2.3	0.4	5.4	2
11	32.8	6.5	1.78	5.1	0.8	4.3	0.8	2.3	0.34	2.2	0.35	4.8	1.9
12	33.4	6.4	1.88	5.1	0.8	4.2	0.8	2.3	0.35	2.4	0.38	4.8	1.9
13	20.2	3.9	1.17	3.2	0.5	2.6	0.5	1.6	0.23	1.6	0.27	2.6	0.6
14	19.6	4.1	1.15	3.2	0.5	2.7	0.5	1.5	0.23	1.6	0.28	2.5	0.6
15	61.1	10.2	2.48	6.7	0.9	4.5	0.8	2.3	0.35	2.4	0.37	4.7	0.8
16	30.5	5.7	1.65	4.5	0.7	3.6	0.7	1.9	0.29	2	0.32	4.2	1.5
17	46.2	8	2.16	6.1	0.8	4.4	0.8	2.3	0.33	2.1	0.33	4.5	1.4
18	51.4	9.1	2.28	6.5	0.9	4.4	0.8	2.4	0.35	2.4	0.38	4.8	1.5
19	36.5	6.5	1.76	5	0.7	3.7	0.7	2.1	0.32	2.2	0.34	3.8	1
20	34.1	6.3	1.79	5	0.8	4.1	0.8	2.1	0.31	2	0.32	4.4	1.4
21	20.2	4.4	1.34	3.8	0.6	3.6	0.7	2.2	0.33	2.3	0.37	3.7	2.2
22	22.3	4.3	1.37	3.9	0.6	3.5	0.7	2	0.31	2.1	0.33	4.2	2.3
23	20.9	4.6	1.43	4.1	0.7	4	0.8	2.3	0.35	2.4	0.38	3.7	2.1
24	32.7	6.1	1.63	4.4	0.6	2.9	0.6	1.5	0.22	1.5	0.25	2.7	0.5
45	64.1	10.7	2.61	7.2	0.9	4.6	0.8	2.2	0.32	2.1	0.36	4.5	0.7
46	49.8	8.6	2.13	5.8	0.8	3.7	0.7	1.9	0.28	1.8	0.29	3.9	0.5

Final Report
Activation Laboratories

Analyte Symbol	W	Tl	Pb	Bi	Th	U
Unit Symbol	ppm	ppm	ppm	ppm	ppm	ppm
Detection Limit	1	0.1	5	0.4	0.1	0.1
1	4	0.2	18	< 0.4	5.3	1.2
2	< 1	0.2	17	< 0.4	4.9	1.1
3	3	0.3	16	< 0.4	6.7	2.1
4	< 1	0.3	18	< 0.4	6.3	2.1
5	2	0.5	20	< 0.4	13	2.6
6	< 1	0.4	20	< 0.4	10.2	2.1
7	2	0.5	27	0.4	23.7	3.7
8	< 1	0.5	25	< 0.4	24.7	3.7
9	4	0.5	28	< 0.4	23.8	3.8
10	< 1	0.5	15	< 0.4	7.3	2.9
11	1	0.4	14	< 0.4	7	2.8
12	< 1	0.5	16	< 0.4	7.2	2.8
13	4	0.2	17	< 0.4	4.8	1.4
14	< 1	0.2	19	< 0.4	5	1.4
15	4	0.5	29	< 0.4	22	3.7
16	2	0.3	14	< 0.4	7.2	2.1
17	< 1	0.5	21	< 0.4	14.3	2.8
18	6	0.7	23	< 0.4	16.3	2.9
19	< 1	0.4	22	< 0.4	10.5	2.1
20	4	0.4	16	< 0.4	8.9	2.5
21	< 1	0.1	11	< 0.4	4.5	1.2
22	2	0.2	13	< 0.4	4.6	1.3
23	1	0.1	16	< 0.4	4	1.1
24	< 1	0.3	8	< 0.4	5	1.4
45	3	0.5	27	< 0.4	23.5	3.6
46	3	0.4	23	< 0.4	18.1	3.1

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Appendix B. XRD Spectrographs

XRD Spectrum - Sample 1
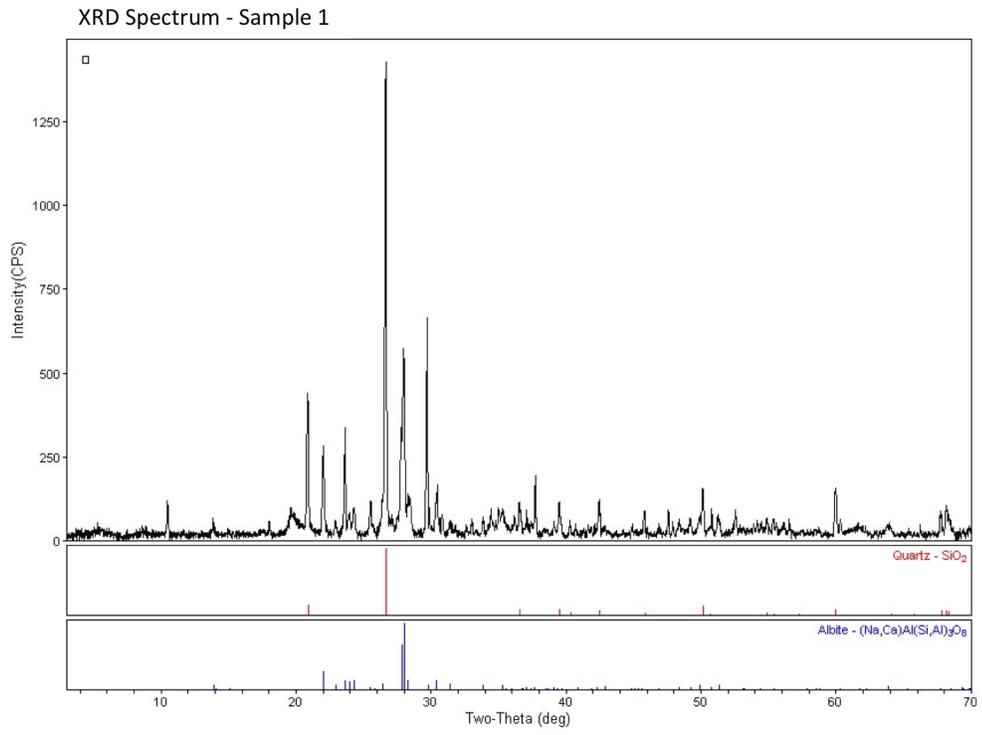
XRD Spectrum – Sample 2
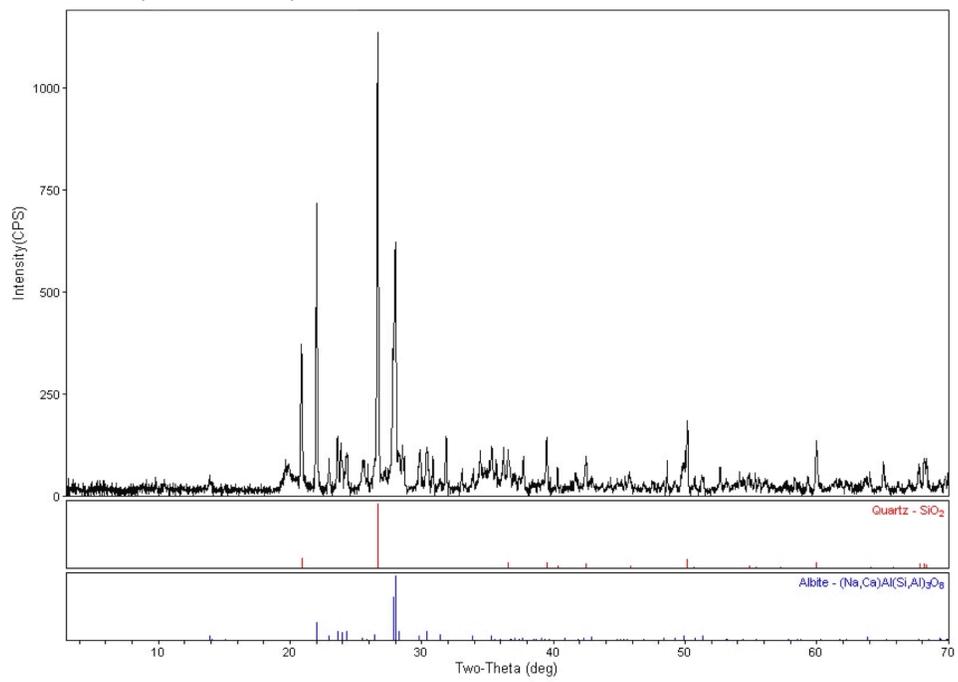

XRD Spectrum – Sample 3
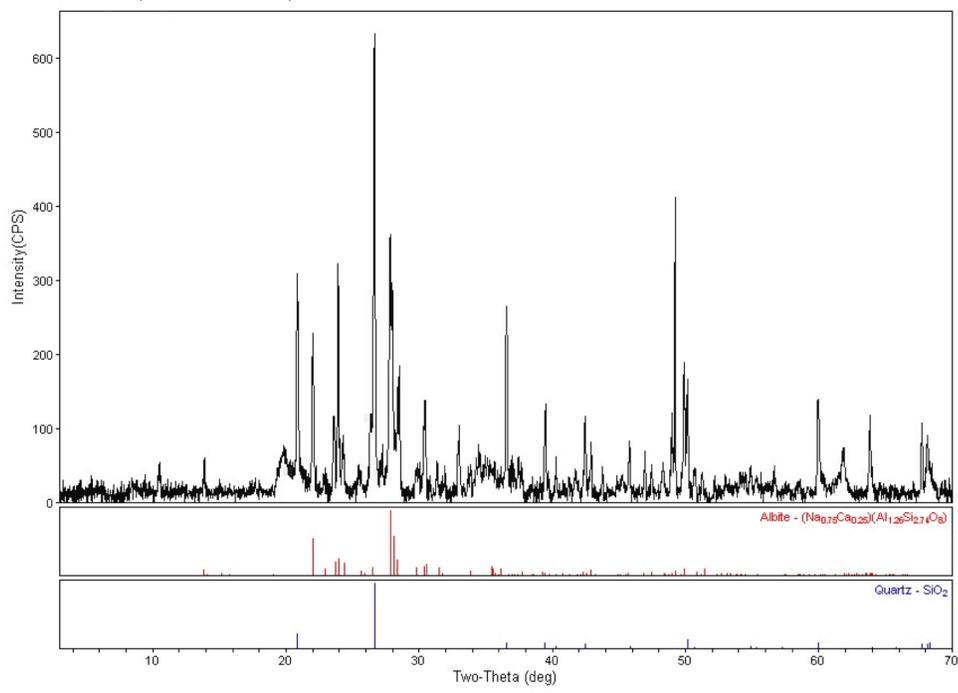
XRD Spectrum – Sample 4
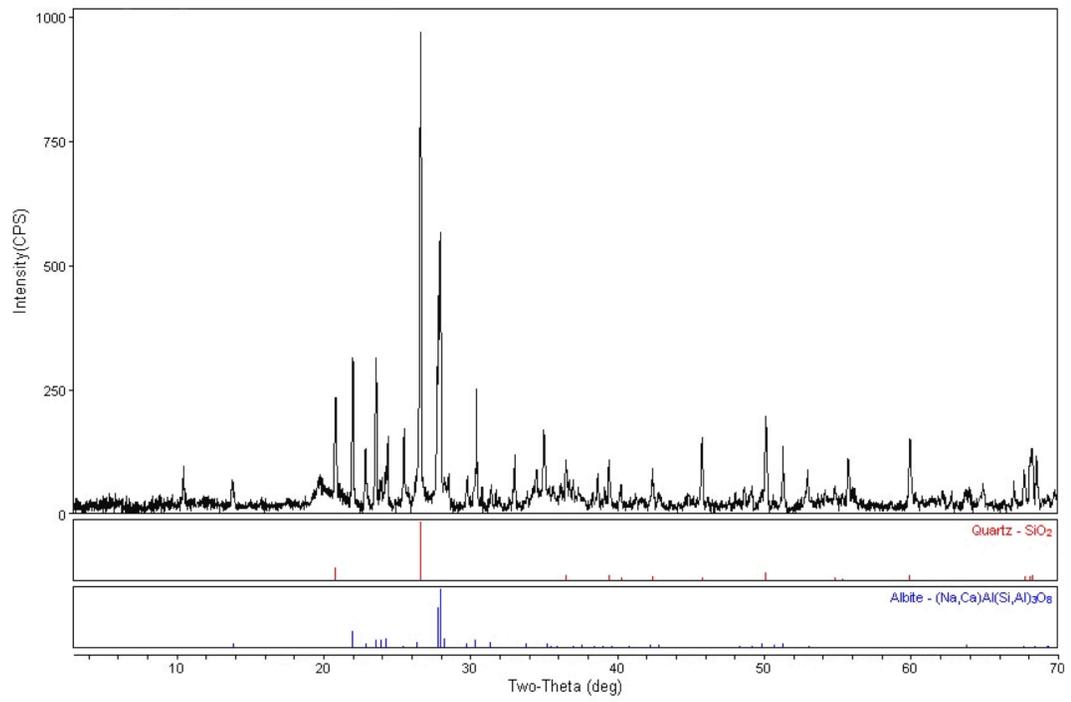

XRD Spectrum – Sample 5
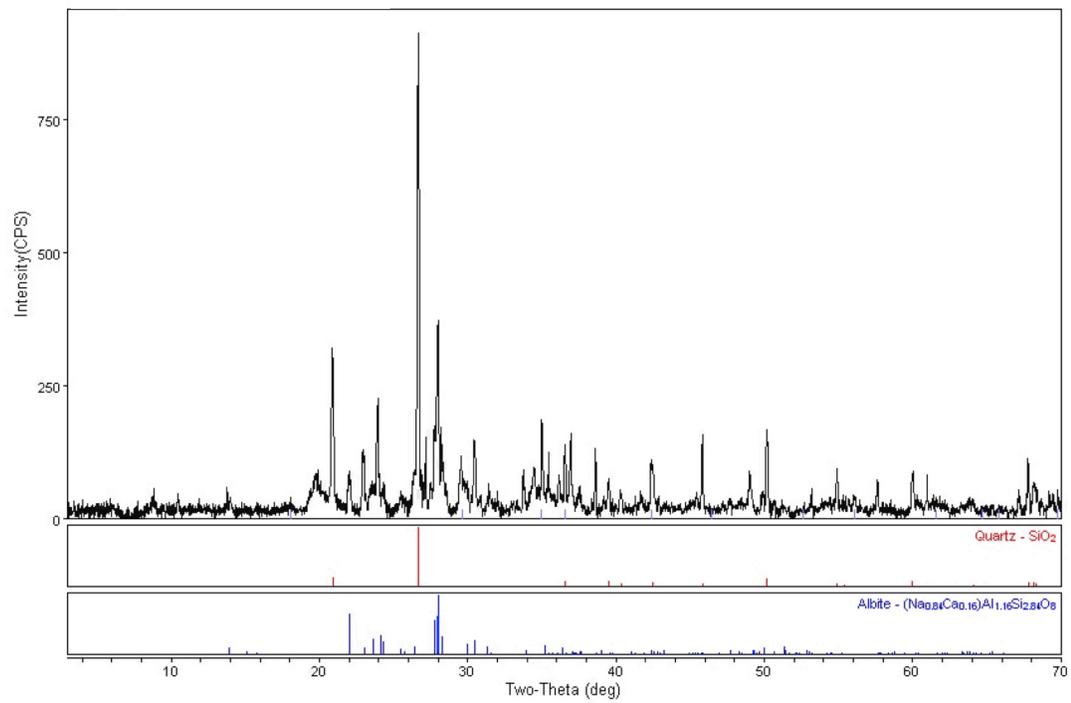
XRD Spectrum – Sample 6
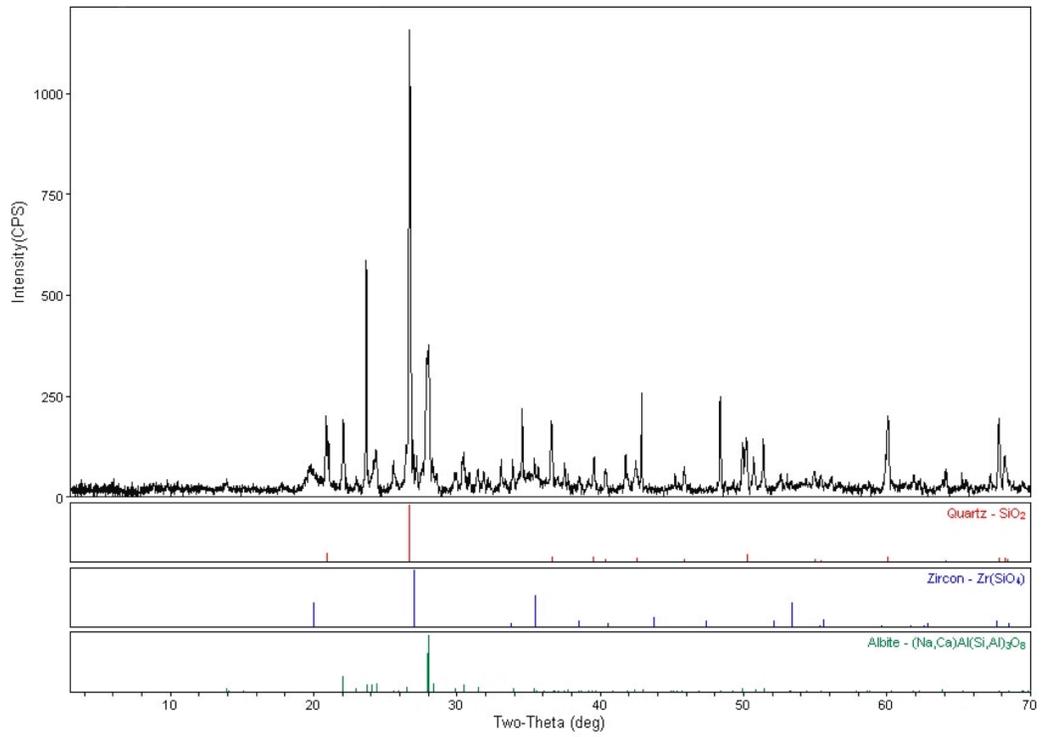

XRD Spectrum – Sample 7
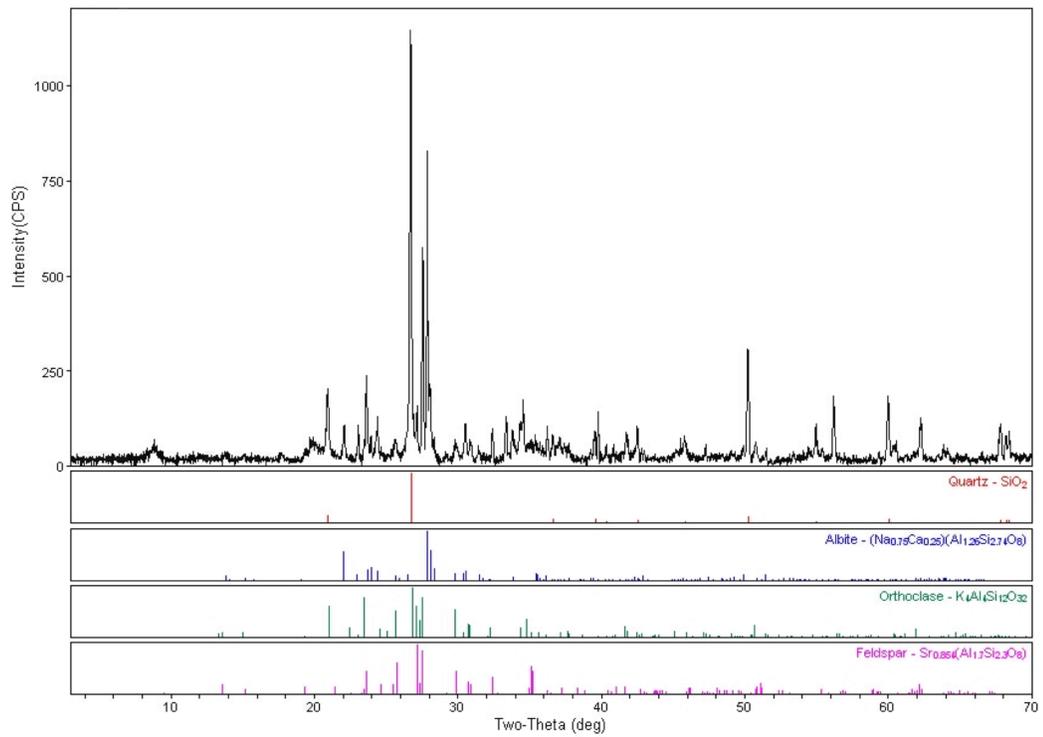
XRD Spectrum – Sample 9
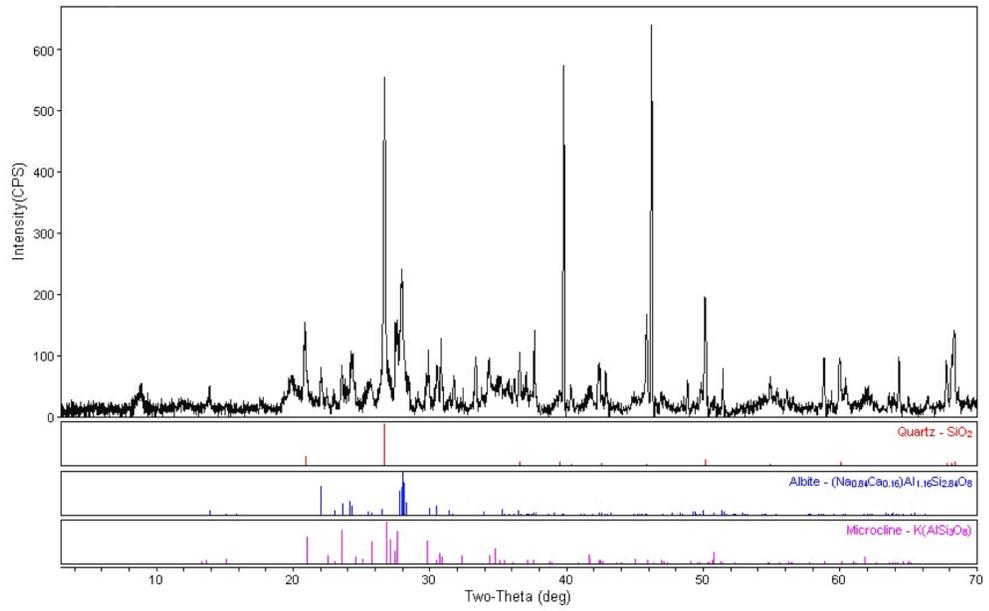
XRD Spectrum – Sample 10
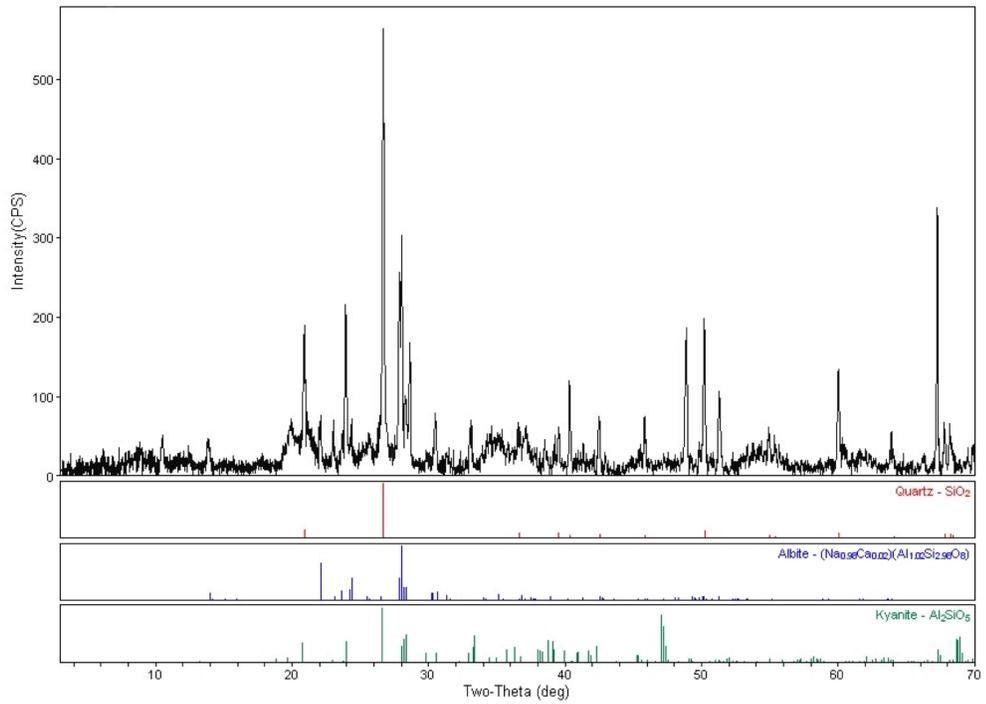
XRD Spectrum – Sample 11
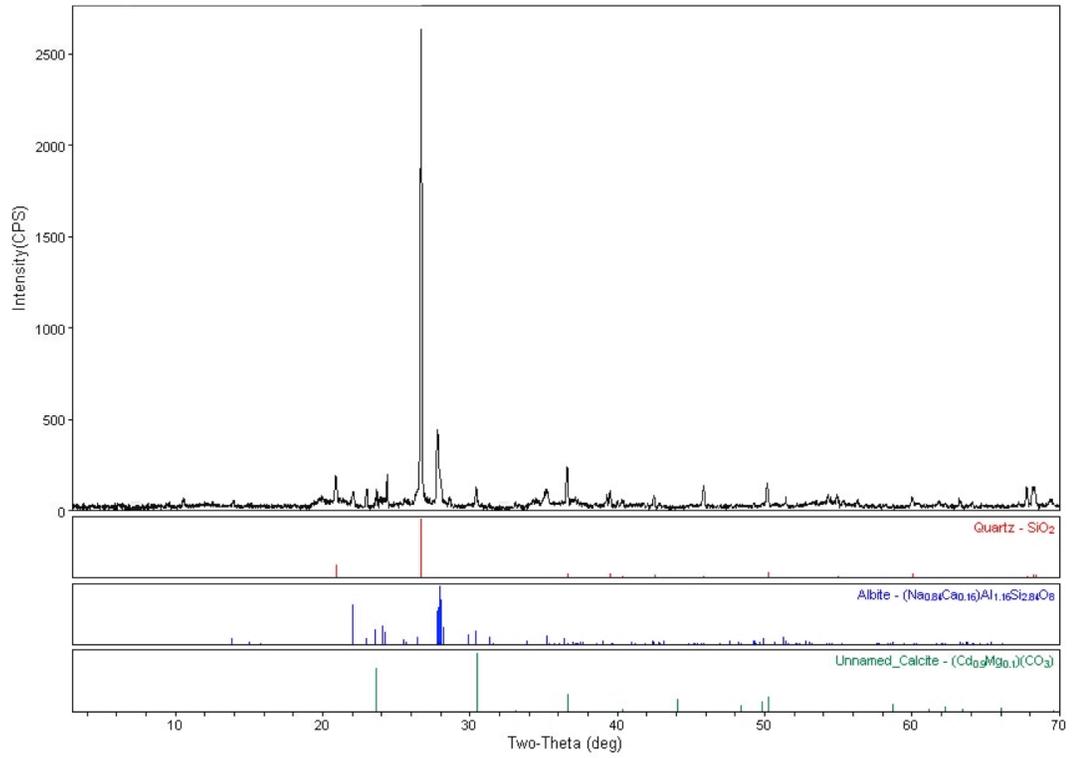
XRD Spectrum – Sample 12
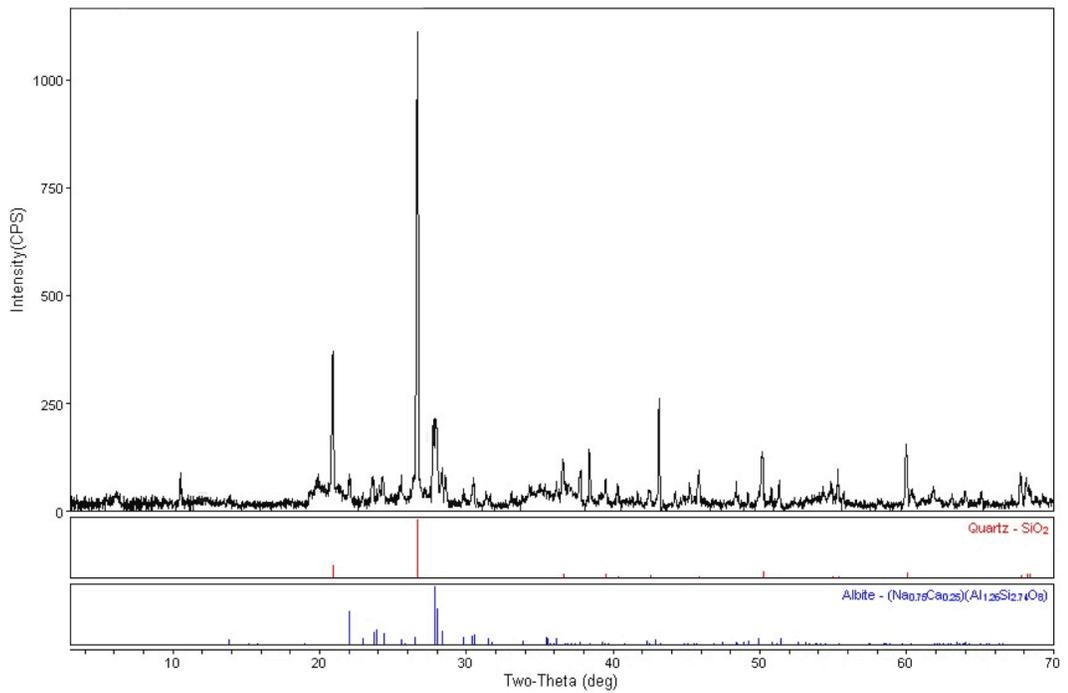
XRD Spectrum – Sample 13
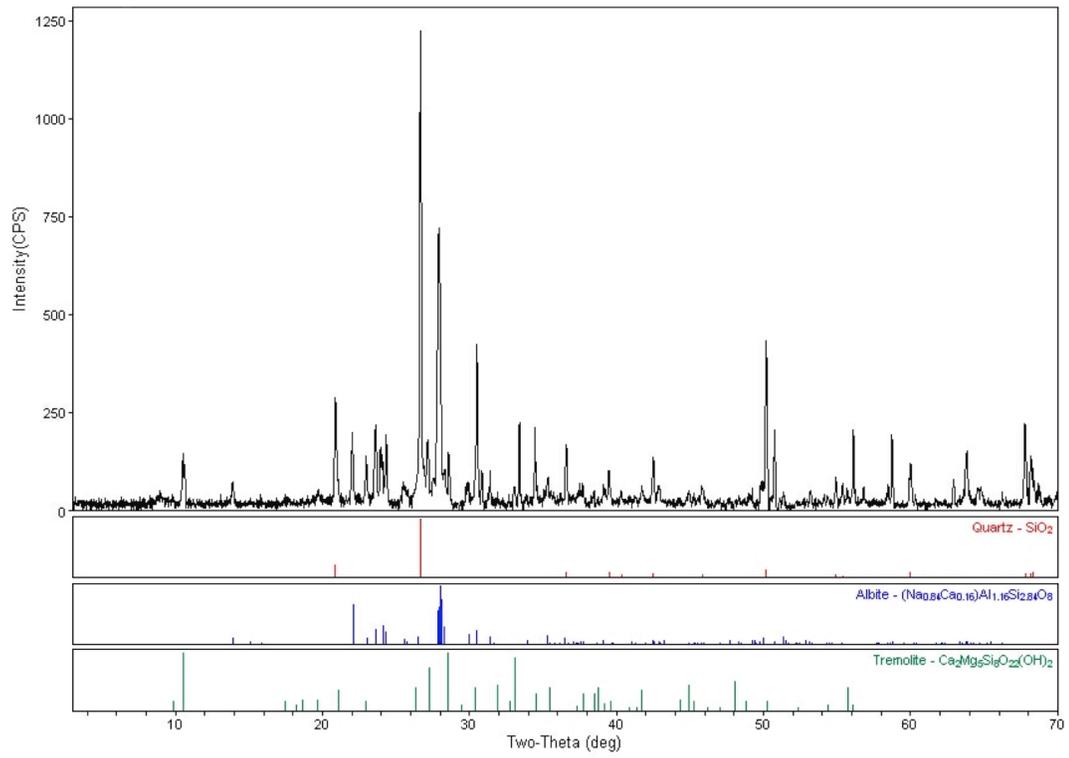
XRD Spectrum – Sample 14

XRD Spectrum – Sample 15

Quartz-alpha - SiO$_2$

XRD Spectrum – Sample 16

Quartz - SiO$_2$

Kyanite - Al$_2$(SiO$_4$)O
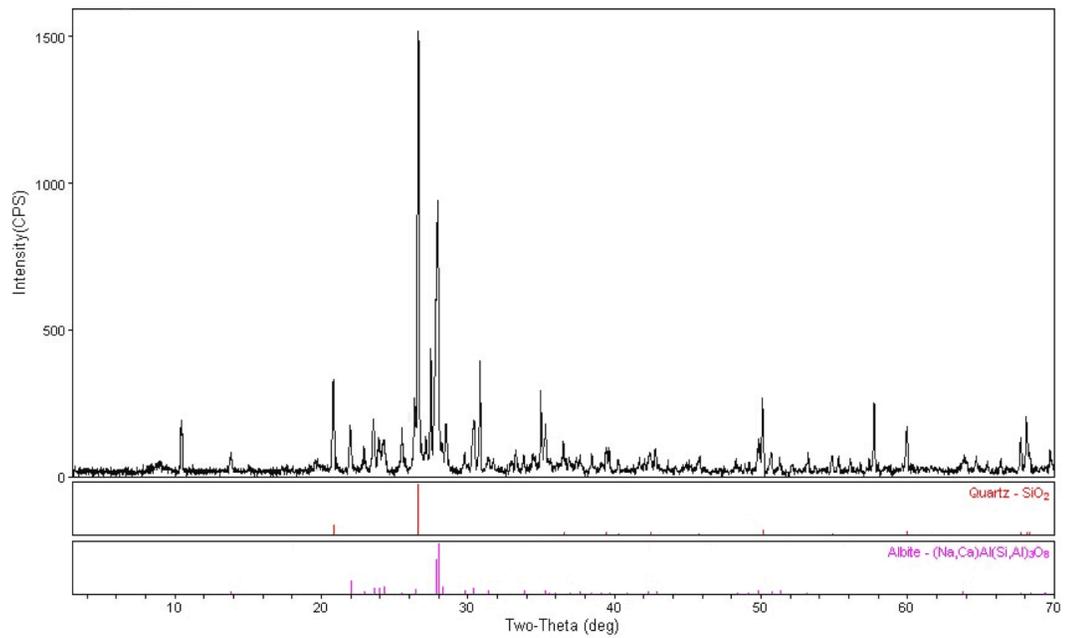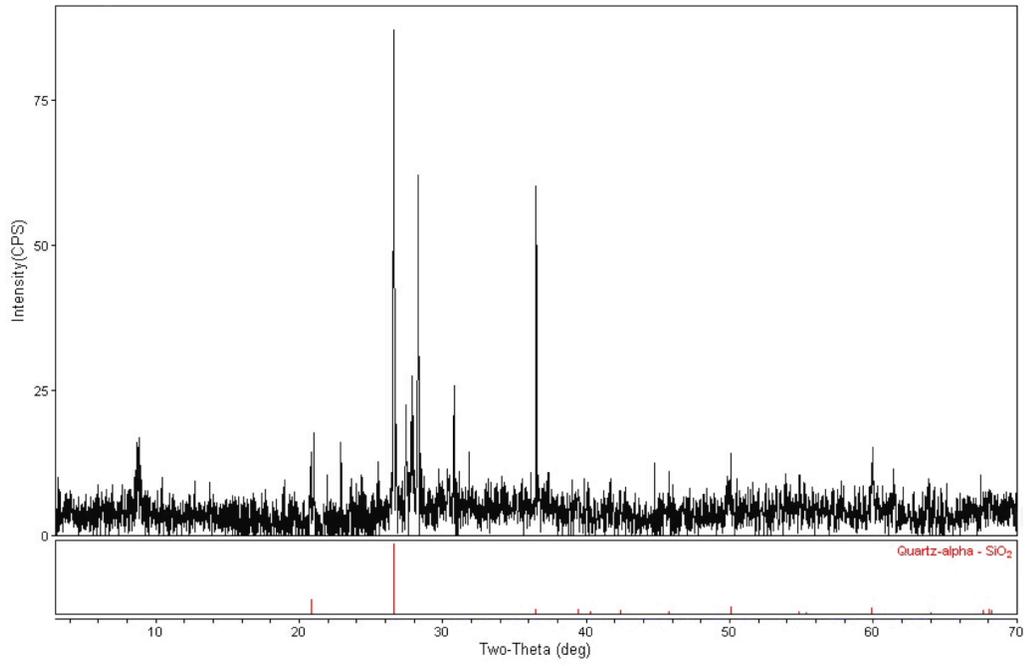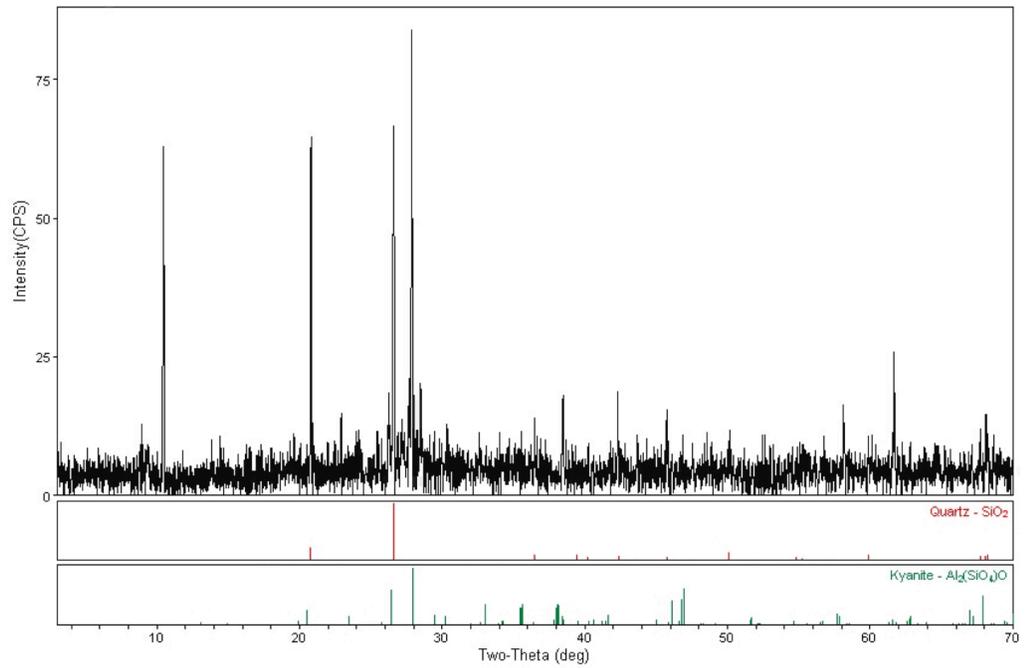
XRD Spectrum – Sample 17
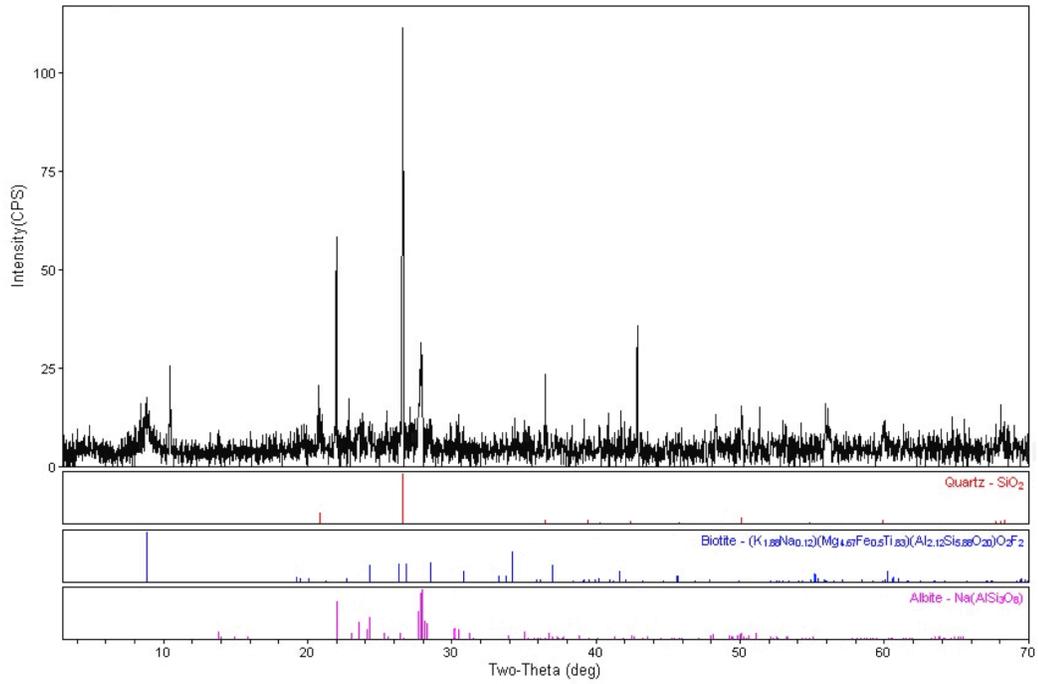
XRD Spectrum – Sample 18
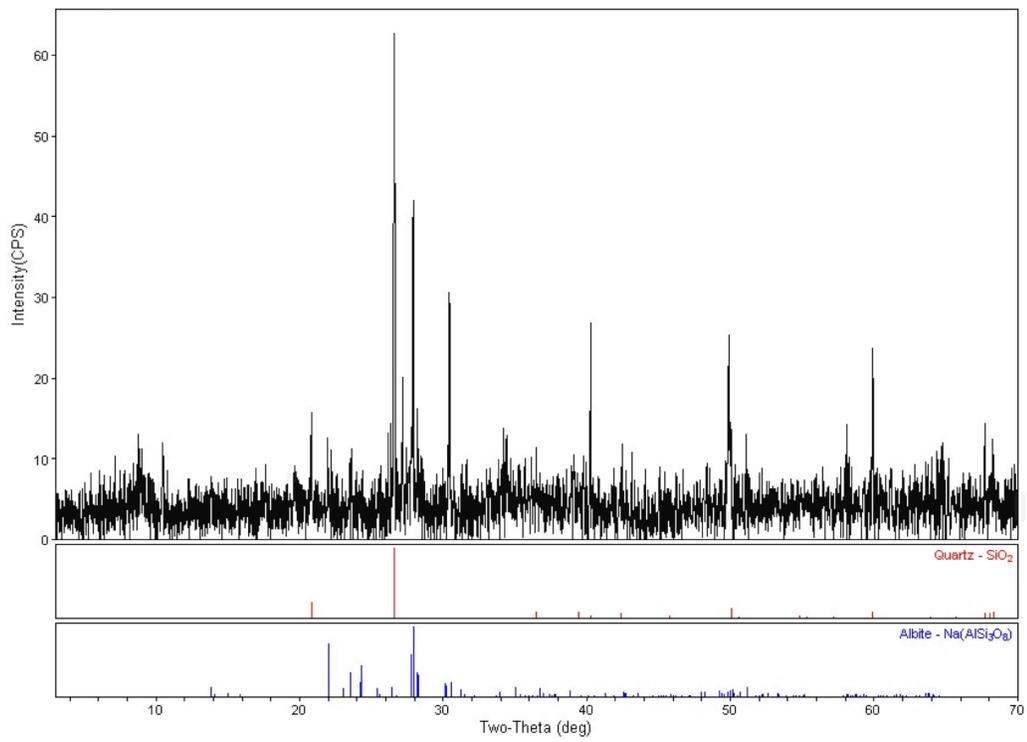
XRD Spectrum – Sample 19
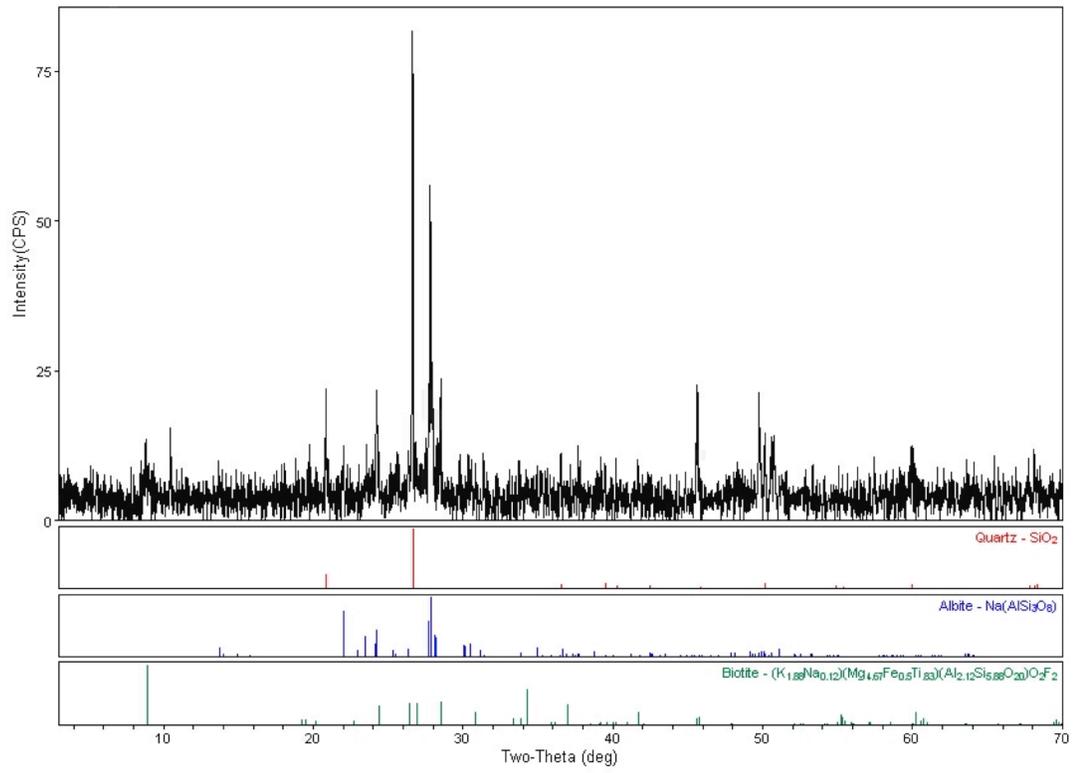
XRD Spectrum – Sample 20
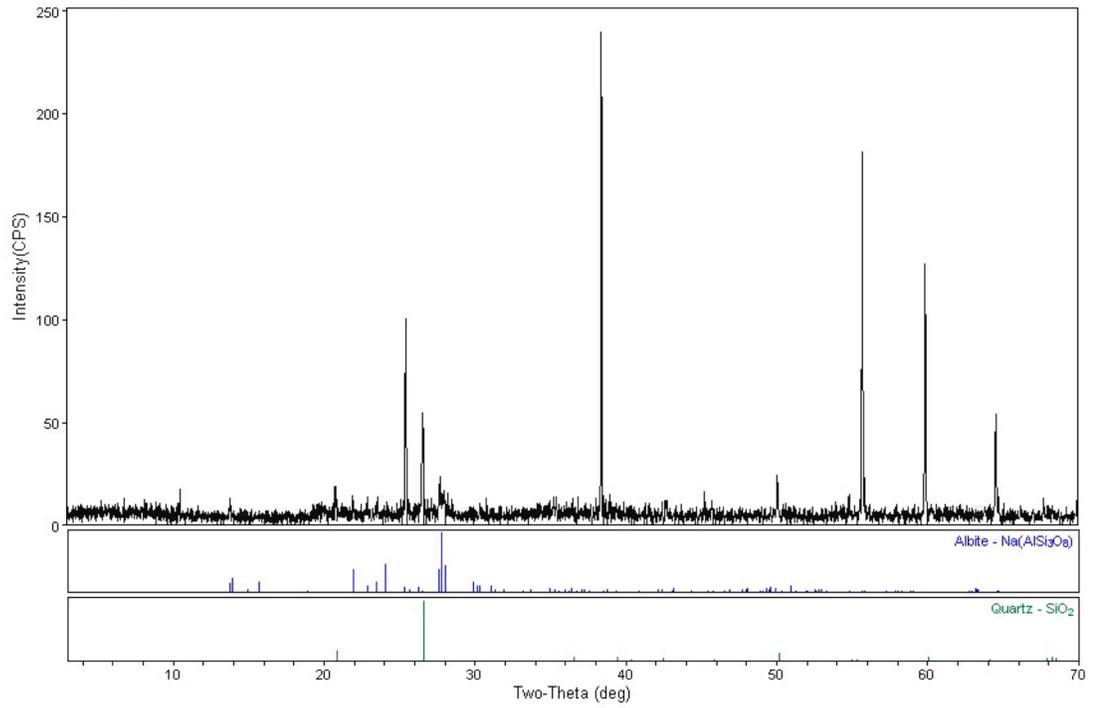
XRD Spectrum – Sample 21
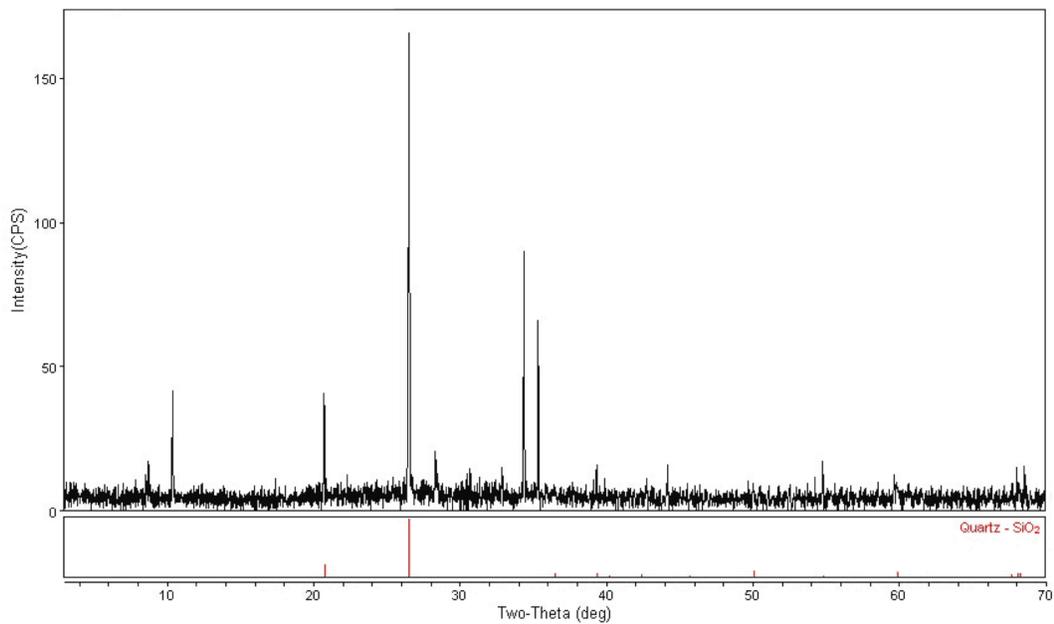

XRD Spectrum – Sample 22
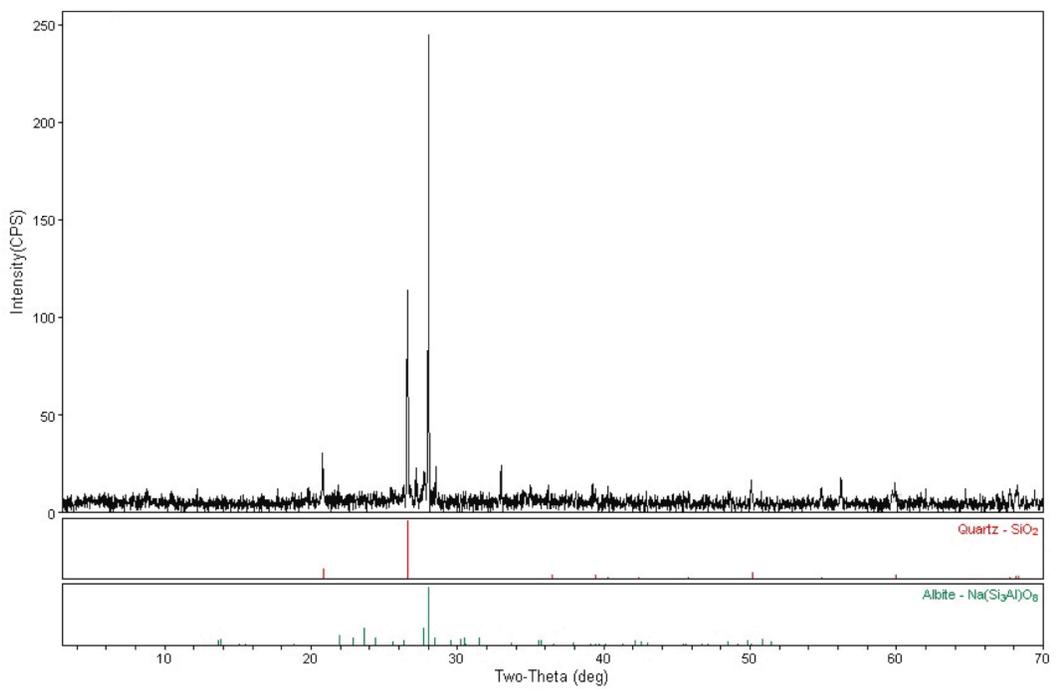
XRD Spectrum – Sample 23
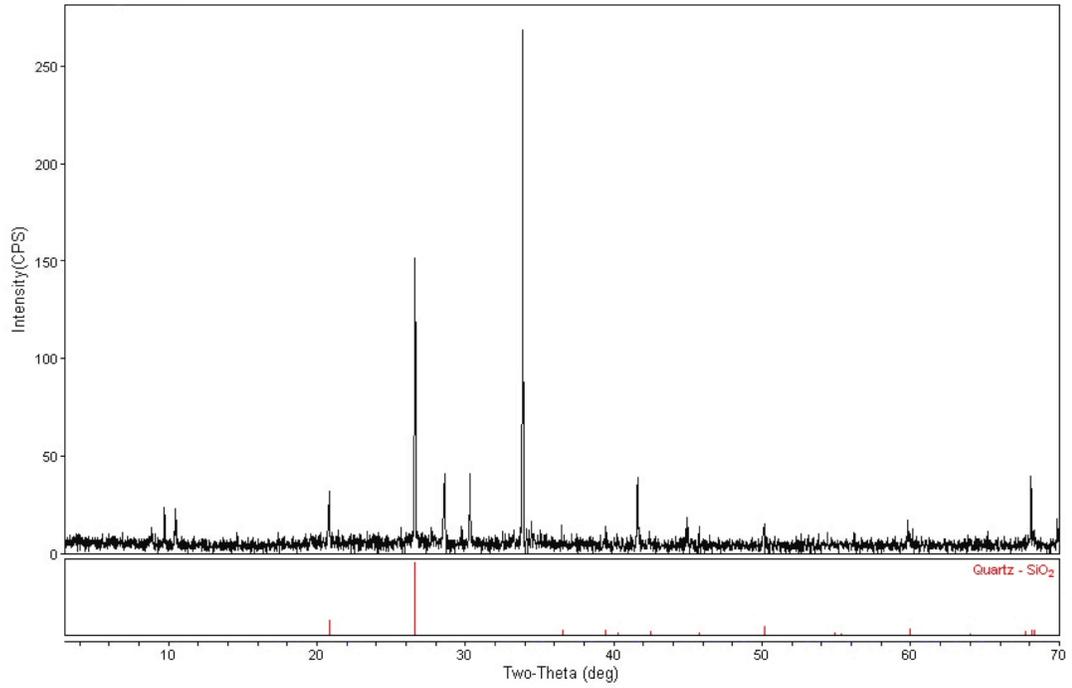
XRD Spectrum – Sample 24
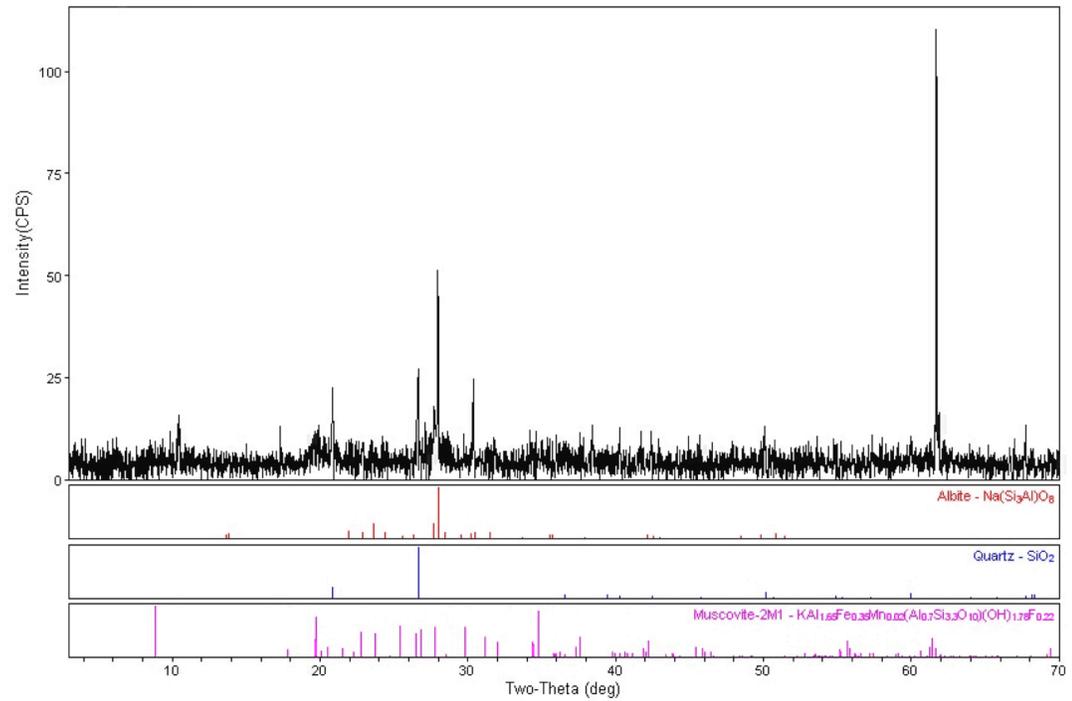
XRD Spectrum – Sample 25
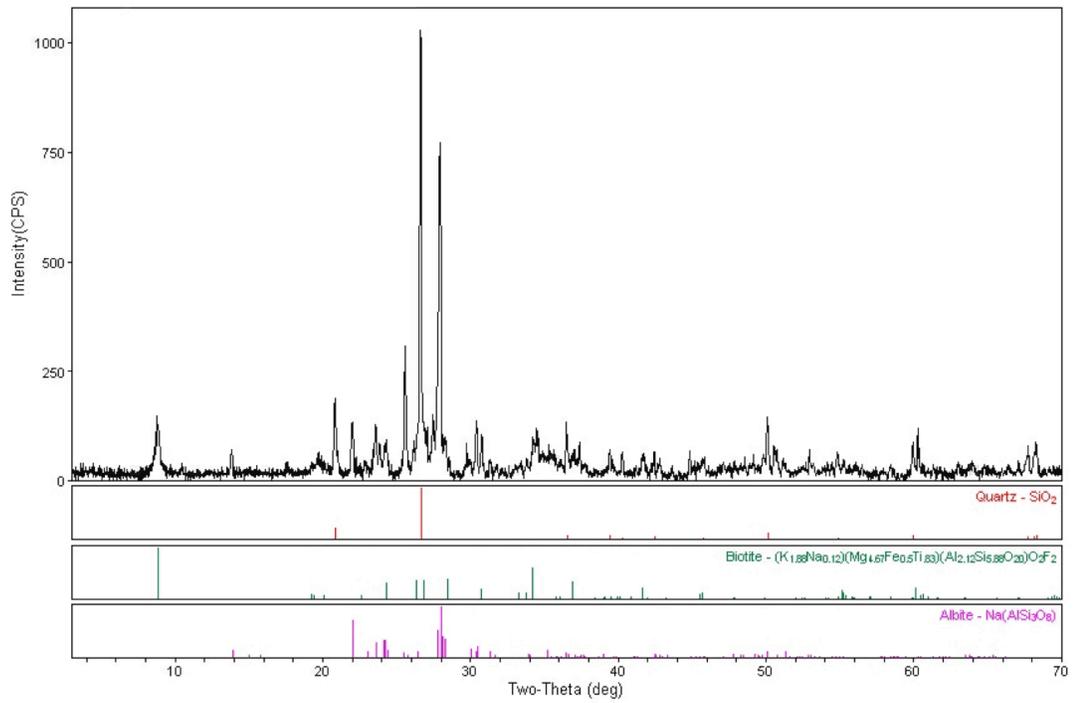
XRD Spectrum – Sample 26

XRD Spectrum – Sample 27

Quartz - SiO$_2$

Calcite - (Ca,Mg)CO$_3$

Albite - Na(AlSi$_3$O$_8$)