CHAPTER 1: INTRODUCTION

INTRODUCTION

Archaeologists and historians have long been interested in identifying trade and exchange networks in the Near East as a means to advance understandings of social and economic interaction during prehistory and antiquity. The chronology of human settlement in the Near East is extensive, spanning the first sedentary communities of the Neolithic to modern times. Studies reconstructing aspects of exchange in this region have used obsidian and ceramics as the key indicators for exchange (Pringle 1986; Yellin, Levy et al. 1996; Blackman and Redford 2005; Healey 2007; Grave, Kealhofer et al. 2009; Khalidi, Gratuze et al. 2009). The chemical characterisation of artefacts enables archaeologists to track their movement through the landscape and thereby elucidate the scale and intensity of local, regional and interregional exchange networks.

This project examines the utility of non-destructive portable x-ray fluorescence (pXRF) analysis of ceramic and obsidian artefact assemblages for archaeological provenancing. A recent addition to the suite of prospective analytic techniques, pXRF offers unique advantages to archaeological scientists including rapid, *in situ*, non-destructive analysis. Non-destructive pXRF has been shown to expand the scope of provenancing studies and provide exciting new insights into social and economic interactions, primarily by facilitating analysis of substantial quantities of artefacts (Jia, Doelman et al. 2010; Mills, Lundblad et al. 2010; Golitko 2011; Sheppard, Irwin et al. 2011) as well as enabling analysis of irreplaceable artefacts, such as those in museum collections which are restricted from invasive analytic techniques (Bonizzoni, Galli et al. 2010; Freitas, Calza et al. 2010; Forster and Grave 2012). The non-destructive nature of pXRF offers clear benefits to archaeological provenancing however, there are also significant methodological challenges associated with accurate analysis and data interpretation with the use of this technique. In addition, there are serious challenges for determining the source of artefacts in the absence of appropriate geological source material.

In this study, the experimental parameters for non-destructive pXRF are evaluated in order to refine the methodology for accurate and precise analysis of archaeological materials. The impacts of these methodological challenges are assessed in case studies of Chalcolithic earthenware ceramics, Chalcolithic obsidian and Byzantine lead glazed ceramics. Building on the pXRF analyses I have undertaken, I explore the use of legacy data and archaeological artefacts to provide comparative geochemical data to enhance sourcing studies. These case studies enable an appraisal of the suitability of non-destructive pXRF for analysis of different artefact classes, and within the context of exchange networks of different scales. The success of pXRF in these preliminary studies highlights its potential as an archaeological tool for providing insights into prehistoric and historic interregional networks and exchange systems in discrete geographic locales.

1.1 Archaeological provenancing

Prehistoric and historic trade and exchange systems linked to a particular artefact class such as obsidian and ceramics can be reconstructed when the material in question has distinctive properties that allow for the geological source to be identified. Early sourcing studies defined similarities in artefact typology to infer trade relationships however, these studies can be enriched by geochemical analysis using techniques such as pXRF (Pollard and Heron 2008; Waksman and Teslenko 2010; Price and Burton 2011). Archaeological provenancing studies using pXRF compare the 'elemental fingerprint' of artefacts with potential geological sources in order to identify the probable origin of artefacts. For this to be possible, the differences in chemical composition between different sources must exceed the differences within a given source material (Huntley 2012). The provenance of artefacts is assigned on the basis their chemical composition is statistically comparable to that of the geological source material. Archaeologists are able to model aspects of interregional exchange networks by examining the frequency and distribution of foreign and locally derived sources of material within assemblages and between sites.

The movement of objects through the landscape is of interest to archaeologists as an indicator of relations between communities. Commensurate with the physical exchange of goods is interpersonal contact and the exchange of intangible cultural markers such as ideology and beliefs. As the primary mechanism for interaction between different cultures, exchange systems are considered a material record of and therefore a proxy for social networks and a platform for the dissemination of cultural traditions, language and technology (Renfrew 1984; Renfrew and Bahn 1991; Robb and Farr 2005; Healey 2007;

Dillian and White 2009). For this reason, Robb (2005) argued that the social links initiated by exchange are of more value than the traded objects themselves. From this perspective, patterns of procurement and distribution observed in provenancing studies can be seen to reflect the greater economic and social landscape.

In order to fully illustrate the geographic boundaries of exchange networks and postulate possible transport routes, provenancing studies require well-contextualised artefacts, geological material from as many potential sources as possible, an analytical method with sufficient sensitivity to differentiate sources and an appropriate data analysis technique that can assign artefacts to sources (eg. Renfrew, Dixon et al. 1968; Gratuze 1999; Johnson, Pearl et al. 2007; Nazaroff, Prufer et al. 2010; Eckert and James 2011; Ma, Zhu et al. 2011). Another component of successful archaeological provenance studies that has only become evident in recent years with the introduction of non-destructive methods is the systematic analysis of large quantities of artefacts. This is particularly beneficial for discerning shifts in geographic and diachronic patterns of exchange (Carter, Poupeau et al. 2006; Carter and Shackley 2007; Carter, Dubernet et al. 2008). The utility of non-destructive pXRF analysis in conjunction with multivariate statistics for reconstructing aspects of obsidian and ceramic exchange networks in the Near East is evaluated against these parameters.

Although provenancing studies ideally require geological samples from all potential sources be analysed, it is not always viable for archaeologists to locate, survey and sample all source deposits due to economic and political constraints. Moreover, analyses frequently reveal the presence of unexpected sources, providing opportunities to identify new sources and thus new aspects of prehistoric human contact (Craig, Speakman et al. 2007; Khalidi, Gratuze et al. 2009; Niknami, Amirkhiz et al. 2010; Forster and Grave 2012). When such cases arise, archaeologists must look elsewhere for geochemical data from potential geological sources for comparative analysis.

The 'Agricultural Revolution' of the Neolithic and the nature of spheres of interaction encompassing the first sedentary communities has been the subject of popular archaeological interest. As the primary indicator for long distance exchange in the prehistoric Near East, obsidian artefacts have been the focus of numerous studies examining exchange during the Neolithic and there is a plethora of trace element analysis for the volcanic outcrops of this region reported in the literature (Gratuze 1999;

Bourdonnec, Delerue et al. 2005; Bressy, Poupeau et al. 2005; Poupeau, Le Bourdonnec et al. 2010). Although the offset between quantitative pXRF and other analytic techniques is well documented (Drake, Nazaroff et al. 2009; Nazaroff, Prufer et al. 2010), there is the potential for this legacy data to be integrated into sourcing studies using pXRF (Forster and Grave 2012). Like obsidian, a substantial body of legacy data has been published for Near Eastern ceramics, however accurate quantitative non-destructive pXRF analysis of ceramics is considerably more problematic and the typically low inter-source variability between clay sources precludes comparison to previous geochemical analysis. On the other hand, archaeological artefacts of known provenance also have the potential to provide comparative geochemical information and thereby enhance our understandings of ceramic procurement and distribution.

Sourcing of obsidian and ceramics contribute to reconstructing aspects of long and short distance exchange in the Near East (Boas 1994; Gratuze 1999; Blackman and Redford 2005; Healey 2007; Khalidi, Gratuze et al. 2009). With a limited number of volcanic sources and a ubiquitous representation in the archaeological record, obsidian represents one of the earliest and most reliable archaeological measures of long distance exchange for this region (Williams Thorpe 1995; Shackley 1998; Balkan-Atli, Binder et al. 1999; Pollard and Heron 2008; Price and Burton 2011). Exchange networks linked to obsidian were initially small and unconnected, but expanded over time and became more complex and converged in the northern Levant and Upper Euphrates valley (Cauvin and Chataigner 1998). With the rise of metallurgy, these exchange systems waned during the Bronze Age.

In comparison, determining the provenance of ceramic artefacts is inherently problematic as not only are there countless potential sediment sources, the chemical signature of ceramics represents the combined product of the clay sediments, the process of levigation and the addition of temper (Stahl, Dores Cruz et al. 2008; Tite 2008; Freitas, Calza et al. 2010; Sterba, Munnik et al. 2012). As a result, systematic studies of ceramic exchange that have identified the geological origin of the entire sample population by and large reflect local or regional networks, classify provenance as ‘local’ vs. ‘non-local’ (Kealhofer, Grave et al. 2010; Wallis, Boulanger et al. 2010), or have a large collection of references samples of known provenance (Mommsen, Mountjoy et al. 2011). Studies reveal that during prehistory, Near Eastern ceramic systems of exchange were generally localised (King, Rupp et al. 1986; Clarke 2001; Grave, Kealhofer et al. 2008) but evolved to comprise complex networks bridging interregional boundaries and consisted of centralised workshops supplying substantial quantities of ceramics to different sites (Pringle 1986; Boas 1994; Charalambous, Sakalis et al. 2010). By elucidating the scale and intensity of local, regional and interregional exchange networks, chemical characterisation of obsidian and ceramics artefacts has the potential to shed light on the economic, social and political relations of past peoples.

1.2 Non-destructive pXRF

PXRF is a tool that offers unique benefits for archaeological provenancing studies relative to other analytic techniques [eg. Neutron Activation Analysis (NAA), Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), Particle Induced X-Ray Emission (PIXE)]. Such portable instrumentation capable of non-destructive analysis provides new opportunities for researchers to undertake analyses on site at excavations and in museums, thereby achieving analytical goals while respecting museum guidelines and national laws with respect to the treatment and export of cultural materials. The rapid analysis times afforded by pXRF and nature of non-destructive analysis minimise time constraints on museum curators and are significant both for negotiating permission to access collections and permitting large quantities of artefacts to be analysed in a practical timeframe.

Although available since the 1970s, innovations in XRF technology in the last decade have produced robust instrumentation capable of completely portable, multi-element, non-destructive analysis, with rapid analysis times and high resolution. The convenience and flexibility offered by contemporary pXRF instrumentation has resulted in its rapid uptake (figure 1) for non-destructive archaeometric investigations including the spatial mapping of artworks (Trentelman, Bouchard et al. 2010), identification of pigments in glazes, inks, paints and rock art (Calza, Oliveira et al. 2010; Powell 2010; Roldán, Murcia-Mascarós et al. 2010; Sendova, Kaiser et al. 2010), and the bulk elemental characterisation of materials including obsidian, basalt, ceramics and glass (Kato, Nakai et al. 2009; Phillips and Speakman 2009; Bonizzoni, Galli et al. 2010; Mills, Lundblad et al. 2010; Burley, Sheppard et al. 2011; Grave, Attenbrow et al. 2011; Polikreti, Murphy et al. 2011; Ikeoka, Appoloni et al. 2012).

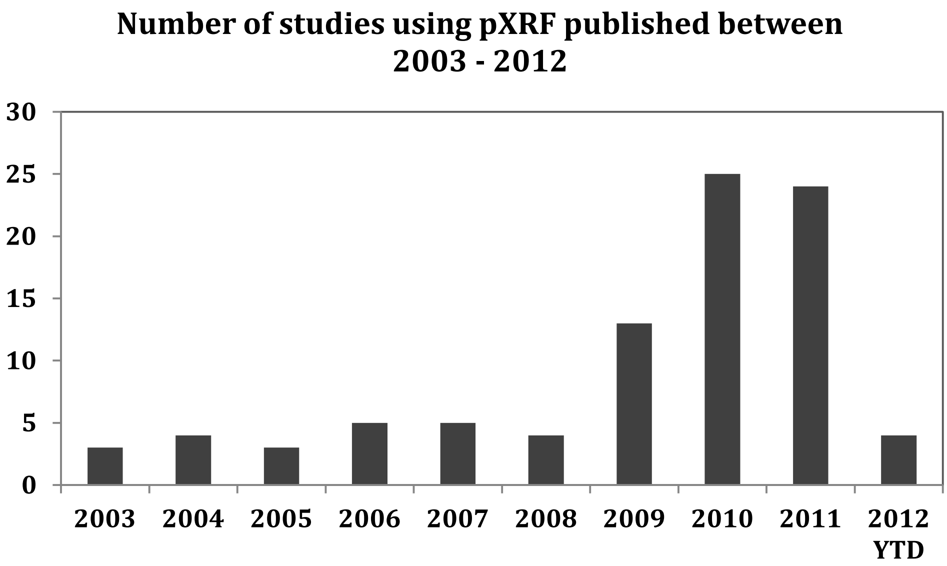

Figure 1: Approximate number of major publications applying pXRF to archaeological artefacts or evaluating aspects of non-destructive analysis[1].

The ease of operation offered by current generation instruments has brought a shift in the way pXRF spectrometers are operated. During the 1990s, pXRF spectrometers were generally run by specialised technicians and the parameters that constrain non-destructive pXRF analysis were well-documented (Maia, Dos Santos et al. 1997; Potts, Webb et al. 1997; Potts, Williams-Thorpe et al. 1997; Ge, Zhang et al. 1998; Shackley 1998). In contrast, since their commercialisation, pXRF spectrometers for archaeological applications have generally been operated by academics and students with minimal background in chemistry and physics (Shackley 2010; Speakman, Little et al. 2011).

The changes to instrumentation in the last decade have had a significant impact on the experimental parameters required to achieve accurate and precise analysis. The most significant alterations to pXRF spectrometers include the introduction of miniature x-ray tubes and superior detector systems and associated electronics, improving analytic sensitivity, and the reduction of the active detection area of the analytic window, bringing commensurate reductions in the relative sample volume analysed (Pantazis, Pantazis et al.

[1] The majority of these studies were published in Applied Radiation and Isotopes, Archaeometry, Journal of Archaeological Science, Spectrochimica Acta B and X-Ray Spectrometry.

2010). However, there has been no empirical analysis in the literature on the effects of surface interferences or grain size and mineralogy on accurate and precise pXRF analysis for current generation instruments. The appropriate application of non-destructive pXRF to archaeological provenancing is a multifaceted process that requires artefacts not amenable to accurate analysis be omitted from the study, methodology that is tailored to the specific artefact class (eg. obsidian or ceramic), and addresses the differential impact of a non-destructive approach on the accuracy of results for various elements (Forster, Grave et al. 2011). Combined with the limited background of many archaeologists in fundamental XRF physics, the absence of published data informing experimental methodology has significant implications for the accuracy of analysis and subsequent interpretation for archaeological provenancing.

The application of non-destructive pXRF to obsidian provenancing can be considered a baseline for the potential of the technique to contribute to reconstructing aspects of trade and exchange. Elemental characterisation is relatively straightforward as the effects of different variables on the reliability of non-destructive pXRF are well established (Shackley 1998; Nazaroff 2009) and there has been comprehensive evaluation of the validity of the technique for sourcing obsidian (Craig, Speakman et al. 2007; Drake, Nazaroff et al. 2009; Nazaroff, Prufer et al. 2010). Subsequently, non-destructive pXRF analysis of obsidian has been applied to a number of large scale sourcing studies (Jia, Doelman et al. 2010; Nazaroff, Prufer et al. 2010; Golitko 2011; Sheppard, Irwin et al. 2011) and various studies have been able to provide insights into aspects of trade and exchange in regions such as Oceania, Russia, China and the Americas with a high degree of confidence (Phillips and Speakman 2009; Craig, Speakman et al. 2010; Jia, Doelman et al. 2010; Burley, Sheppard et al. 2011).

The accuracy of quantitative non-destructive pXRF analysis of ceramics has not faced a comparable level of scrutiny, which has had implications for the scope of archaeometric investigations of ceramics using the technique. Although studies have assessed the validity of quantitative non-destructive pXRF for ceramic sourcing by comparing the compositional groupings identified using non-destructive pXRF with those identified by invasive techniques such as ICP and NAA (Padilla, Espen et al. 2006; Goren, Mommsen et al. 2011), there have been questions raised regarding the potential of commercially manufactured pXRF instruments to generate accurate results and discriminate compositional groupings with high resolution (Speakman, Little et al. 2011). Relative to obsidian, the application of non-destructive pXRF has been limited for archaeological provenancing of ceramics. It has predominantly been employed in response to specific archaeological questions that can be answered by the presence of multiple compositional groupings (Papachristodoulou, Oikonomou et al. 2006; Emery and Morgenstein 2007; Freitas, Calza et al. 2010), except where the geology of local clay sources has distinct geochemical markers (Morgenstein and Redmount 2005; Bonizzoni, Galli et al. 2010; Papachristodoulou, Gravani et al. 2010; Frankel and Webb 2012).

1.3 Research Aims

The focus of this project was to evaluate the utility of non-destructive pXRF analysis for reconstructing aspects of obsidian and ceramic exchange networks in the Near East. In order to make this evaluation, the following questions were addressed:

- What are the parameters for reliable non-destructive pXRF analysis of archaeological obsidian and ceramics?
- Does non-destructive pXRF analysis discriminate between different geological sources accurately and precisely? Does this differ for obsidian and ceramics?
- In the absence of comparative geological material, how can appropriate geochemical data from potential sources be obtained for provenance determination?
- Are obsidian and ceramics suitable indicators for exchange on local, regional and interregional scales?
- How can museum collections be incorporated into large scale studies of the circulation of materials in prehistory and history using non-destructive pXRF?

1.4 Thesis outline

This thesis consists of three articles that explore the potential of non-destructive pXRF analysis to elucidate aspects of trade and exchange networks and avenues for source attribution. These articles advance the established methodology for non-destructive pXRF using current generation instruments, and use case studies to demonstrate the wider utility of non-destructive pXRF for archaeological provenancing. Each article is followed by a short summary relating the findings of the article to the research questions listed above. The success of pXRF in these preliminary studies highlights its potential as an archaeological tool for providing insights into systems of exchange.

In Chapter Two, '*Non-destructive analysis using PXRF: methodology and application to archaeological ceramics*' (Forster, Grave et al. 2011), the impact of interferences related to the physical properties of artefacts (mineral heterogeneity, organic deposits and non-planar surface morphology) are empirically evaluated in order to develop a methodology for applying non-destructive pXRF analysis to analysis of archaeological materials. The cumulative impact of these interferences on the accuracy and precision of analysis is examined using Chalcolithic earthenwares from Turkey. The case study in this paper specifically addresses the complexities of non-destructive pXRF analysis of ceramics, however the methodological findings are equally relevant to other artefact classes, including the analysis of obsidian, basalt, glass and rock art (Grave, Attenbrow et al. 2011; Huntley 2012). The case study demonstrates that with an appropriate methodology, non-destructive pXRF analysis of archaeological ceramics can reliably distinguish geochemical groups of differing provenance.

Chapter Three, '*Non-destructive analysis of museum-curated obsidian from the Near East*'(Forster and Grave 2012), addresses the potential for legacy datasets from invasive analytic techniques (ICP, XRF) to provide comparative geochemical data for sourcing obsidian artefacts. Using geological obsidian from central Anatolia, it is demonstrated that quantitative non-destructive pXRF can be integrated with and compared to legacy datasets where there is sufficient inter-source variability. Non-destructive pXRF analysis of obsidian artefacts from the excavation sites of Tell Brak, Mersin-Yümüktepe and Tell Arpachiyah indicates that during the Chalcolithic, East Göllü Dağ and Nenezi Dağ continued to the major sources of obsidian to communities in central Anatolia and the Bingöl range and mountains surrounding Lake Van supplied sites east of the Levant. This study in particular underscores the potential for non-destructive pXRF analysis of museum collections to make significant contributions to understandings of obsidian circulation.

In Chapter Four, '*Lead leaching effects on non-destructive pXRF analysis of Byzantine lead glazed ceramics*', the impact of spectral interferences introduced by lead leaching on the sensitivity of non-destructive pXRF using Byzantine lead glazed ceramics excavated from

Polis tis Chrysochous, Morphou and Ayia Kiriakos, Cyprus are evaluated. It is evident that spectral interferences do not necessarily prevent discrimination of sources. Archaeological artefacts of known provenance are evaluated as a potential source of comparative geochemical data for determining the likely provenance of ceramics, however systematic differences in production precluded their value as a source of comparative geochemical data for the Byzantine wares.

CHAPTER 2: NON-DESTRUCTIVE ANALYSIS USING PXRF: METHODOLOGY AND APPLICATION TO ARCHAEOLOGICAL CERAMICS

2.10 Research Implications

"Non-destructive analysis using PXRF: methodology and application to archaeological ceramics" specifically aimed to address the first research question set out in the introduction, "what are the parameters for reliable non-destructive pXRF analysis of archaeological obsidian and ceramics?" This first step was necessary to ensuring the reliability of subsequent analyses of obsidian and ceramic artefacts in this research project. The experimental parameters and constraints of the technique were identified by classifying surface properties that render an artefact unamenable to accurate analysis, determining the experimental requirements for precise analysis of matrices ranging from very-fine grained to medium-grained, and identifying the most reliable elements reported. The developed methodology was demonstrated to achieve accurate and precise results even for earthenware ceramics, which may be considered a "worst case scenario" for the application of non-destructive pXRF for archaeological provenancing.

Relative to destructive analytic techniques, non-destructive pXRF generates reliable data for comparatively few diagnostic elements. Even so, non-destructive pXRF of the earthenware ceramics was able to discriminate between geological sources with high sensitivity. This may be a result of the mineralogically rich nature of earthenware ceramics. Further analysis is required to evaluate if this sensitivity is reproducible and non-destructive pXRF can accurately and precisely distinguish compositional differences for other types of ceramics.

Non-destructive pXRF analysis of the Chalcolithic earthenwares reveals significant compositional variation within clay sources on a local scale. Such high levels of intra-source variation may have implications on the capacity of the technique to identify compositional groupings with high resolution when there are a greater number of sources represented in a dataset, as may occur in studies exploring long distance exchange. In such a case, it is likely there will be considerable overlap in the compositional range of sources. Nevertheless, when a discrete number of sources are present, non-destructive analysis of earthenware ceramics discriminates between compositional groups with high resolution.

2.11 Statement of Authors' Contribution

We, the candidate and the candidate's Principal Supervisor, certify that all co-authors have consented to their work being included in the thesis and they have accepted the candidate's contribution as indicated in the *Statement of Originality*.

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2.12 Statement of Originality

We, the candidate and the candidate's Principal Supervisor, certify that the following text, figures and diagrams are the candidate's original work.

Type of work	Page number/s
Text	13-22
Figure 1	16
Figure 2	16
Figure 3	18
Figure 4	19
Figure 5	22

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CHAPTER 3: NON-DESTRUCTIVE PXRF ANALYSIS OF MUSEUM-CURATED OBSIDIAN FROM THE NEAR-EAST

3.8 Research Implications

Obsidian is considered ideal for provenancing studies in the Near East as sources are homogeneous and there are only a discrete number of potential sources in the region. Furthermore, obsidian is an ideal material for archaeological provenancing using non-destructive pXRF. It requires few - if any – replicate measurements, the most reliable elements for non-destructive pXRF are incompatible elements (Rb, Sr, Y, Zr and Nb) that typically vary between volcanic outcrops, and knapped obsidian frequently has areas with a smooth surface. Although non-destructive pXRF has inferior resolution than destructive analytic techniques, this is not a limiting factor as intra-source compositional variability is generally substantially lower than the inter-source variability. Subsequently, it is possible to discern different geological sources with a high resolution using relatively few diagnostic elements.

It is well established in the literature that obsidian is a suitable indicator for long distance exchange. The findings of "Non-destructive pXRF analysis of museum-curated obsidian from the Near East" indicate that obsidian also has potential to shed light on localised systems of exchange. Studies of short distance exchange necessitate analysis of complete assemblages of neighbouring sites in order to elucidate patterns in procurement and distribution. It should be noted the rapidity of non-destructive pXRF does facilitate such large scale analysis.

It is possible to integrate legacy data published in the literature into studies using non-destructive pXRF in order to ascertain the provenance of unknown sources. As a result, even in the absence of comparative geological material, the source attribution of Near Eastern obsidian artefacts in museum collections is a relatively straightforward process. This is a significant finding as it indicates that analysis of individual collections can be used in conjunction with other studies to make important contributions to understandings of obsidian distribution and procurement.

3.9 Statement of Authors' Contribution

We, the candidate and the candidate's Principal Supervisor, certify that all co-authors have consented to their work being included in the thesis and they have accepted the candidate's contribution as indicated in the *Statement of Originality*.

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Type of work	Page number/s
Text	27-35
Figure 1	28
Figure 2	30
Figure 3	33
Figure 4	34

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CHAPTER 4: LEAD LEACHING EFFECTS ON NON-DESTRUCTIVE PXRF ANALYSIS OF BYZANTINE CYPRIOT LEAD GLAZED CERAMICS

4.9 Research Implications

Non-destructive pXRF analysis of lead glazed ceramics presents a number of challenges for archaeological provenancing. Not only do surface properties and matrix heterogeneity condition the parameters of analysis, the spectral interferences introduced by lead leaching further reduce the number of diagnostic elements reported.

The potential for the findings of this study to contribute to answering the stated research questions definitively is somewhat limited as a number of variables are impacting the results. It would be preferable to first evaluate the accuracy and precision of non-destructive pXRF for identifying compositional groupings of finewares relative to an invasive technique such as NAA; then second assess the implications of a reduced number of diagnostic elements on the technique's potential to distinguish these groups.

It is evident that multivariate analysis identified compositional differences between ceramics known to be of different provenance, however it is not clear if the observed groups reflect production from a single region with significant intra-source compositional variation, or if there are subsets within the groups of ceramics produced from different clay sources. In either case however, the wide spread of the results indicates that when multiple sources are present in a study, clearly distinguishing discrete groups can be problematic given the suite of elements available using non-destructive pXRF. This has implications for the utility of non-destructive pXRF for exploring short and long distance exchange.

Compared to obsidian, source attribution of ceramics is considerably more challenging in the absence of comparative geological material. Even using a well-validated calibration algorithm specific to the matrix of the ceramics in question, the small compositional differences between compositional groups has negated the usefulness of legacy data for the samples examined. Multivariate analysis in "Lead leaching effects on non-destructive pXRF analysis of Byzantine lead glazed ceramics" shows that reference materials with a similar matrix is required for comparative analyses. With such reference material from which to infer provenance, it is possible to incorporate museum collections of ceramics into larger scale studies of ceramics exchange.

4.10 Statement of Authors' Contribution

We, the candidate and the candidate's Principal Supervisor, certify that all co-authors have consented to their work being included in the thesis and they have accepted the candidate's contribution as indicated in the *Statement of Originality*.

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Type of work	**Page number/s**
Text	40-65
Figure 1	42
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Figure 4	51
Figure 5	52
Figure 6	58
Figure 7	59

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CHAPTER 5: CONCLUSION

CONCLUSION

In this thesis, I have critically evaluated the utility of non-destructive pXRF analysis for reconstructing aspects of obsidian and ceramic exchange networks in the Near East. A novel methodological approach for non-destructive pXRF was developed through empirical evaluation. This methodology was further scrutinised through its application to the analysis of three distinct archaeological materials, demonstrates its broad utility in generating accurate and appropriate data to address archaeological questions. Innovative avenues for expanding provenancing studies are presented, with case studies exemplifying the potential of museum collections to significantly increase the scope of studies investigating interregional exchange. The demonstration that legacy data is a valid source of comparative data is a substantial contribution to sourcing studies and has incredible potential for enhancing obsidian provenancing in other parts of the world. The application of pXRF to different artefact classes (obsidian and ceramics) and the resulting data's contribution to archaeological understandings of both large and small scale exchange networks has been explored through the work presented in this thesis.

Non-destructive pXRF analysis of experimental matrices and Near Eastern artefacts contributed to critically evaluating the technique's capacity for reliable analysis of obsidian and ceramics and application to archaeological provenancing. The sample characteristics typical to archaeological samples that impact non-destructive analysis involve a range of factors including surface morphology, surface coatings, grain size and matrix mineralogy (Van Grieken and Markowicz 2002; Gigante, Ricciardi et al. 2005; Potts and West 2008; Liritzis and Zacharias 2010). Without appropriate modification to experimental procedures and data analysis, these interferences are likely to produce substantial data inconsistencies. The protocols developed for managing these potential interferences and thereby conditioning reliable non-destructive pXRF for current generation instrumentation were delineated in Chapter Two. The parameters of permissible surface morphology for accurate analysis were defined, the requisite number of analyses for precise analysis quantified, and the most reliable elements specified. Using Chalcolithic earthenware ceramics from Turkey, the reliability of this methodology for non-destructive pXRF was evaluated. This case study demonstrates that the cumulative impact of potential interferences do not necessarily preclude accurate and precise measurement. That is, when artefacts unamenable to analysis are omitted from the study and appropriate methodology is applied during analyses, non-destructive pXRF has the potential to discriminate between compositional groups with high sensitivity. The developed methodology is relevant to a range of material types, including obsidian and ceramics, and has been applied to subsequent artefact assemblages in the latter case studies of this thesis.

Although the accuracy and precision of non-destructive pXRF analysis is comparable for obsidian and ceramics when an appropriate methodology is applied, the efficacy of the suite of elements reported for provenancing is substantially different for these two artefact classes. Obsidian provenancing studies are able to distinguish different volcanic sources with high resolution using only two or three variables (typically the incompatible elements Rb, Sr, Zr or Nb) (Shackley 1998; Gratuze 1999; Carter, Dubernet et al. 2008). Likewise, non-destructive pXRF has the capacity to identify compositional groups with high resolution for the same suite of elements (Craig, Speakman et al. 2007; Nazaroff, Prufer et al. 2010). In comparison, ceramic provenancing studies commonly apply multivariate statistics to a wider range of diagnostic elements and artefacts from the same source typically represent a wider range of geochemistry (Baxter, Beardah et al. 2008; Fermo, Delnevo et al. 2008; Michelaki and Hancock 2011). For pXRF analysis of ceramics, Speakman (2011) provides evidence that even with partially destructive sample preparation, the effects of fewer measureable elements and low resolution relative to destructive techniques are detrimental to distinguishing compositional groups. The surface interferences and spectral interferences discussed in Chapters Two and Four further reduce the quantity of diagnostic elements measured and although not apparent for the Chalcolithic earthenwares from Anatolia, this may have significant implications for the potential of non-destructive pXRF to discriminate compositional groups for ceramics from other regions.

The capacity, or lack thereof, of an analytic technique to accurately and precisely identify compositional differences has significance for its potential application to studies investigating exchange networks of different scales[2]. In various parts of the world,

[2] Matsumoto (2010) recently suggested that it is not appropriate to define 'short' and 'long' distance exchange according to geographic distance as distance is a relative concept influenced by the topography of the region, social conditions and technology available. However, for the purpose of this thesis it is appropriate to approximate a definition for different scales of exchange. In a seminal paper, Renfrew (1968) proposed

numerous studies have shown that non-destructive pXRF of obsidian is a reliable indicator for long distance exchange (Craig, Speakman et al. 2007; Phillips and Speakman 2009; Nazaroff, Prufer et al. 2010; Burley, Sheppard et al. 2011). The findings of the Chapter Three study suggest that for the Chalcolithic Near East, the usefulness of obsidian may also be broadened to include reconstructions of localised procurement and systems of distribution. Non-destructive pXRF analyses of obsidian from Tell Brak, Tell Arpachiyah and Mersin-Yümüktepe indicate there were substantial differences in procurement and distribution strategies for sites that were geographically proximate.

In comparison, systematic geochemical analysis of ceramics has been most relevant to reconstructing localised systems of exchange or inferring changing trade relationships based on the proportion of non-local sources present in an assemblage (Grave, Kealhofer et al. 2009; Boileau, Badre et al. 2010). The sheer number of clay sources from which the ceramics may have been derived is problematic for identifying provenance, and the compositional variability of ceramics potentially renders the capacity of multivariate analysis to differentiate sources inadequate. As yet, non-destructive pXRF of ceramics has had limited application to determining the provenance of ceramics, except where local clay sources have been identified on the basis of distinct geochemical markers (Morgenstein and Redmount 2005; Bonizzoni, Galli et al. 2010; Papachristodoulou, Gravani et al. 2010; Frankel and Webb 2012). In Chapter Two, non-destructive pXRF reliably differentiated geographically proximate clay sources. It is unclear, however, whether non-destructive pXRF has the accuracy and precision to clearly discriminate compositional groups on a wider geographic scale. In Chapter Four, it has been shown that there is considerable compositional variation in the identified groups and it is not possible to verify the accuracy or precision of these groups due to a lack of comparative data. These findings indicate that pXRF analysis of obsidian and ceramics present different potentials for contributing to, and interpreting modes of, exchange in the Near East. Lazzari et al (2009) recently combined geochemical analysis of obsidian and ceramics to demonstrate that multiple socio-economic networks co-existed in northwestern Argentina during the Formative period and observed that social interaction between sites was not always reflected by both artefact

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that those within the 'supply zone' (approximately 200 km) were willing to travel to the source to procure obsidian and those further away in the 'contact zone' obtained obsidian via down-the-line exchange. For this paper, 'short distance', or localised exchange, is defined as within approximately 200 km. It is noted these boundaries may vary considerably for ceramics.

classes. For the Near East, this highlights the importance of integrating multiple material classes for holistic understandings of spheres of interaction and mechanisms for exchange.

In the absence of direct geological comparator material, archaeologists must look to other sources for reference geochemical data. The two options discussed in this thesis are legacy data and archaeological samples of known provenance. In Chapter Three, multivariate analysis of legacy data extracted from the literature and archaeological artefacts is demonstrated to accurately distinguish between geochemical groups. Although there is a slight offset between data generated using pXRF and other techniques, multivariate analysis identifies geochemical groups with a high degree of confidence when there are distinct geochemical differences. Source attribution for ceramics is substantially more difficult in the absence of reference controls. Quantitative non-destructive pXRF analysis of ceramics is problematic and high intra-source variability precludes comparisons to legacy data. As exemplified in Chapter Four, semi-quantitative analysis necessitates appropriate reference material that reflects contemporary manufacturing practices for accurate comparative analysis. Not only does variation in levigation and temper affect the elemental signature of ceramics, non-destructive pXRF is sensitive to variable material properties including the fabric porosity and density.

Non-destructive pXRF offers unique advantages to archaeological provenancing studies as it facilitates access to museum collections and the substantial body of previously unanalysed artefacts they represent. In isolation, analysis of museum collections poses challenges for data interpretation within an archaeological context. However, where analysis of small sample populations can be combined into a larger, integrated dataset, it is possible to examine shifts in patterns of procurement and distribution strategies, as exemplified by a series of obsidian studies at Çatalhöyük (Carter, Poupeau et al. 2006; Carter and Shackley 2007; Carter, Dubernet et al. 2008). The case studies in Chapters Three and Four emphasises the potential for non-destructive pXRF analysis of museum collections of artefacts to make a valuable contribution to understandings of exchange networks. Reconstructing aspects of exchange systems requires artefacts to be well-contextualised and in many cases, there is no information describing the stratigraphic or spatial context of museum-curated artefacts. For the collections analysed in Chapters Two and Three, the chronological data in archival records is sufficiently precise to enable general patterns of material procurement and distribution to be elucidated.

In Chapter Three, non-destructive pXRF analysis of the obsidian collection housed at the Nicholson Museum substantially increased the quantity of published data for obsidian dating to the Chalcolithic. The model of obsidian procurement and distribution which is broadest in scope for the Chalcolithic Near East is based on small numbers of artefacts for each site (Coqueugniot 1998). In part, by contributing to the growing body of data for the Chalcolithic, this study addresses the lacuna in understanding of obsidian circulation during this period in the Near East. The results indicate that East Göllü Dağ and Nenezi Dağ continued to be the major sources of obsidian to communities in central Anatolia, and obsidian from the Bingöl ranges and deposits surrounding Lake Van continued to be the major sources to sites east of the Levant. Distinct variations in the proportions of obsidian sources in the analysed assemblages suggest multiple exchange systems existed and varied between nearby sites.

In Chapter Four, non-destructive pXRF enabled analysis of lead glazed ceramics excavated from north-west Cyprus and provided new insights into a region of Cyprus largely overlooked in previous studies on eastern Mediterranean exchange during the Byzantine period. The provenance of the majority of ceramics excavated from the sites of Morphou and Polis tis Chrysochous in north-west Cyprus are attributed to the two major workshops operating during this period, Paphos and Lapithos, on the basis of their typology, chronological context, lead glaze composition, and geochemistry of the ceramic matrix. A small number of artefacts thought to be Levantine imports are present in the assemblages. With only a small sample population, it is not possible to make unequivocal conclusions regarding the archaeological implications of the ceramics in this study. However, the results support previous research that found there were minimal ceramics imported to Cyprus and the majority of glazed ceramics were produced locally in organised workshops (Megaw and Jones 1983; King, Rupp et al. 1986; Pringle 1986; Gregory 1987; King 1987; Charalambous, Sakalis et al. 2010). This is in contrast to the excavations of crusader sites in the Levant from which lead glazed ceramics have been excavated representing both imports and local workshops (Pringle 1985; Boas 1994; Milwright 2003; Blackman and Redford 2005; Stern 2008).

These preliminary investigations into trade and exchange networks in the Near East during the Chalcolithic and Byzantine periods suggests that exchange networks linked to different artefact classes were largely separate and operated along different trade routes. During the

Chalcolithic, the Anatolian earthenwares analysed in this study were produced from local clay sources while in comparison, the obsidian excavated from Tell Brak, Tell Arpachiyah and Mersin-Yümüktepe was transported significant distances. Obsidian procurement and distribution dwindled with the rise of metallurgy, however ceramic exchange networks continued to function and over time expanded and became more complex. During the Byzantine period, these networks encompassed the entire Mediterranean and included extensive land and maritime trade routes.

5.1 Future Directions

Non-destructive pXRF offers unique advantages to archaeological provenancing studies. While lacking the resolution and measureable elements of invasive techniques, its capacity for portable, non-destructive analysis is invaluable for preserving the integrity of artefacts for future archaeometric investigations and facilitating studies of previously inaccessible museum collections. However, the potential for non-destructive pXRF for reconstructing aspects of exchange networks in the Near East currently remains unrealised. The success of these preliminary case studies is indicative of the potential of non-destructive pXRF for archaeological provenancing and furthering understandings of past human behaviour in this region.

The benefits of non-destructive pXRF analysis are most obvious and well established for obsidian, where volcanic deposits are geochemically distinct, there are a discrete number of potential sources, and quantitative analysis is straightforward, enabling accurate source attribution via comparison to legacy data. There is incredible potential for non-destructive pXRF analysis to dramatically enhance the scope of obsidian sourcing studies in the Near East and examine shifts in spatial and diachronic patterns of procurement. By analysing obsidian that is curated in museum and research institutions from the entire region, it will be possible to advance theories of mechanisms for exchange, identify the boundaries of interregional interaction and determine spatial variation in exchange networks. Systematic characterisation of Near Eastern obsidian spanning the Neolithic to the Bronze Age and identifying shifts in procurement and distribution would enable an in-depth analysis of the evolution of obsidian exchange networks and connection to economic, social, political and technological changes underscoring these shifts.

Ceramics were ubiquitous throughout the prehistoric and historic Near East. If non-destructive pXRF can be shown to reliably identify compositional groups for earthenwares and finewares in larger datasets and with the use of appropriate comparative material, it could potentially facilitate analysis of ceramics curated in a number of museum and other research collections. By incorporating such findings into conceptual models of exchange based on obsidian and ceramics provenancing, there is the incredible opportunity for archaeologists to further explore the nature of spheres of interaction, and the aspects of social complexity that result in different procurement strategies.

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