A History Cast in Stone:
Geochemical Chert Sourcing Using Portable X-Ray Fluorescence (PXRF) in Southern Ontario

by

Jennifer Cullison

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Author’s Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.
Abstract

To test the validity of portable X-Ray Fluorescence (PXRF) for chert sourcing, 32 chert artifacts from the Waterloo Region Museum in southern Ontario were compared to 56 chert source samples. The use of PXRF in archaeology, due to its lower energy outputs in comparison to lab based XRF devices, has raised questions about the method's validity. Since chert has such a wide range of internal elemental variation, methods of chemical analysis are difficult. The PXRF used for this study was an Olympus Vanta C Series with a silver anode X-ray tube with the Geochem (3-Beam) mode. The artifacts where geochemically classified using discriminant analysis as well as macroscopically identified. The two modes of sourcing had a match at a rate of 76%. The findings suggest that the PXRF may be helpful in determining chert sources, but it should be used in addition to visual identification. There are many potential pitfalls such as an insufficient number of source samples or statistical error that need to be considered when archaeologists attempt studies of this nature.
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Chapter 1

Museums provide one of the most direct ways of forming emotional connections between the public and archaeologists (Merriman 2004; Wahlgren and Svanberg 2008; Weil 1997). By nurturing these connections, archaeologists are uniquely positioned to form stronger connections with the public. The concept of the public can be defined in numerous ways, and it is constantly shifting (Weil 1997, 257). For my purposes, I will be defining the public as a general public or at least the portion of the general public that attends museums. According to a survey by Ramos and Duganne (2000, 21), 88 percent of adults in America have visited a museum with archaeological material at least once in their lives. McManamon (1991) suggests there are three categories that the general public belong to in terms of their interest in archaeology. The first consists of the deeply interested who may go out of their way to read published studies. This group is the smallest by far. The second group is a bit larger, and they may go out of their way to read an article or visit an excavation. The third group, by far the majority of the general public, gets their archaeological information from incidental exposure such as the nightly news, Indiana Jones, or museums. Pearce (1990, 133) provides a similar grouping for the three types of publics who attend museums; this includes people with no commitment to the past, people who are informed about and interested in the past, and children. Individual museums will have a different subset of this public that they will engage with directly. There are many museums that focus on specific subject matter such as cultural groups. For this study, artifacts come from the Waterloo Region Museum which, as the name suggests, focuses on the region of Waterloo. This means that the public my research affects is the Waterloo community. With these definitions of the public in mind, I will answer the question of how my research may influence this public.

The “museum” as a concept arose in Europe some two hundred years ago as a means for the wealthy elite to boast to the larger public and it ultimately acted as a tool for shaping public perception (Weil 1997). Essentially, museums have acted from the beginning as a tool to shape the public’s view of artifacts and by association their respective culture of origin. What you label an artifact with affects how the public will interpret the artifact (Thomas 2010, 8). If the interpretation of the artifact changes over time the label must then be continuously updated. In the 19th and 20th centuries, these labels were often strongly influenced by nationalism (Wahlgren and Svanberg 2008, 242).

It was in a museum that Christian Jürgensen Thomsen first developed the notion of the three-age system for European archaeology, consisting of the Stone age, Bronze age, and Iron age (Wingfield 2017). His access to a large set of artifacts from numerous sites allowed Thomsen to develop connections that had not been previously visible. The archaeologists excavating one site at a time had microscopic views in comparison to Thomsen. All the artifacts had to be put together in order for greater connections to become apparent. Following in Thomsen’s footsteps, John Lubbock took these classifications further and developed the concepts of Paleolithic and Neolithic (Wingfield 2017). He too was able to accomplish this by the comparison of collections in a museum. These categorizations forever changed our perspective of the past and the way we view the development of human industries. While these categorizations were vital to the advancement of archaeology, they show a trend of the elite interpreting for the general public by way of controlling the narrative. In the last century, there has been a notable shift from curation of objects by the wealthy elite to experts (Weil 1997). Moreover, where museums used to hold positions of control, they now act in service of the public (Merriman 2004; Wahlgren and Svanberg 2008; Weil 1997).

However, over the past century, archaeology has pulled away from museums. The divorce of these two fields began in the 1920s as archaeologists moved from museums to the modern research
university (Thomas 2010, 6; Wingfield 2017, 603). The purpose of many of the early 20th century’s major excavations was to fill museums, but this has long since stopped as archaeology’s goal (Wingfield 2017, 601). Present day archaeology is no longer a quest for treasure but a more wholistic approach to uncovering how ancient peoples lived through scientific survey and excavation practices. At the time of the separation of the fields, this shift in archaeology’s goals was at odds with that of the museum. Museums at the time are often depicted as passive repositories for the artifacts that archaeologists have excavated (Siwan 2007, 12). They were simply places that hold the ‘evidence’ that supports the claims of the archaeologist (Merriman 2004, 87; Wingfield 2017, 603). In this role, they preserve, display, and interpret artifacts for the public. In essence, museum curation is often considered a separate enterprise from that of archaeology. However, in recent decades, the goal of the museum has shifted as well. As museums evolve to focus more on the desires of the general public, the types of artifacts they value have shifted as well (Wahlgren and Svanberg 2008). Despite this, the rift between the fields remains.

This begs the question, then, as to what should be done about this separation. Nicholas Thomas (2010, 6) suggests that archaeologists must frame “the museum as method”. He notes how the simple act of labeling and organizing artifacts can lead to accidental discovery. After all, this is what Thomsen and Lubbock were able to do. When the artifacts from sites all over a given region and time-period are brought together, the more widespread connections can be visible in a way that is not possible when everything is looked at in parts. This process can be made difficult by the separation of the artifacts in some of the earliest museum collections from their contexts. These collections have been decontextualized or may have never been given proper contextual information from the start (Swain 2007, 92). It is thought that the concept of collections should be instead viewed as assemblages (Wingfield 2017, 595). In the world of museums, a collection is a set of artifacts that were put together by a curator often because they have some trait in common such as cultural affiliation or they tell some sort of story. Archaeologists use the term assemblage to describe roughly the same thing. In archaeology, an assemblage has two general meanings, a group of objects connected by similar traits (e.g., being made of the same material or a shared stylistic similarity) and a group of objects that share the same context (e.g., the same archaeological site or chronological phase) (Hamilakis and Jones 2017, 77). Essentially, the term collection is used by museums while assemblage is an archaeological term. What Wingfield (2017) is then suggesting is the reconciling of these two terms to help span the void between the two fields. Even artifacts that have lost their original contexts can now be viewed in their new context. In this way, my research at the Waterloo Region Museum, described in the following chapter, ties into this narrative. The collection I utilized for my analysis contains artifacts that were collected throughout Waterloo region from contexts now forgotten. Collections are based on the perspective of the collector, and they are influenced by what the collector valued (Wahlgren and Svanberg 2008, 248). In this way, my study will be influenced not only by the choices of the Indigenous peoples but by those of the man – Jacob Stroh – who collected the artifacts.

The artifacts I used for my research certainly have strong ties to the Waterloo region. They were donated by Nathaniel C. Stroh to the Waterloo Historical Society, who then donated them to the Waterloo Region Museum. These artifacts were not collected by Nathaniel Stroh but by his father, Jacob Gaukel Stroh. Jacob Stroh was born September 25, 1848, in Berlin, now Kitchener, Ontario, and starting in 1871, his occupation would be listed as a tanner in the census (Jacob Gaukel Stroh 2001). While he may have been officially a tanner, his legacy is not greatly connected to his occupation. Stroh spent much of his free time collecting Indigenous artifacts and also obtained them from those who frequented his tanning business (Stroh 1957). He asked farmers to be on the lookout for artifacts as they tilled the soil in their fields and in return Stroh would tan a small skin such as that of a raccoon for
free (Stroh 1957). In later years he would simply discount the tanning costs or pay for the artifacts outright (Stroh 1957).

Jacob Gaukel Stroh died on May 23, 1935, at 86 years old (Jacob Gaukel Stroh 2001), and was buried in the Mount Hope Cemetery in Kitchener. Twenty-two years later, in 1957, Nathaniel Stroh donated approximately 700 artifacts collected by his father. The echoes of his life are seen throughout the Waterloo and Kitchener communities. The artifacts used in this study are pieces of Indigenous history, but they are also pieces of Jacob Stroh’s legacy of collecting and the Region of Waterloo’s history.

It is unfortunate that these artifacts have been inaccessible to the public as they sit in collections. The difficult job of the curator involves the selection of artifacts that are deemed ‘good’ or ‘representative’ (Thomas 2010, 7). The 32 artifacts included in my study would not often fall into these categories as they were removed from the archaeological record by Jacob Stroh without proper documentation. If these artifacts are instead framed as an assemblage of their own right, my attempts to learn more about them then adds depth to our understanding. In this way, my modest sourcing study is a step in this direction.

Today, the public dictates what it wants to see in museums (Merriman 2004; Weil 1997), and a majority of museums cater to the wants of the public in an effort to draw them in. One of the most effective ways to reach the public has proven to be a focus on community and heritage. Weil (1997) discusses how communities might use museums as a tool to tell their stories. Presently, museums are more successful than ever with more visitors and stable funding than they have received in past centuries (Thomas 2010, 6). In western countries one can find a museum in nearly every town and several in every city (Swain 2007, 6). Archaeology must meet the people where they are, and it has to make them care, which is why the need for public education about archaeology, including local heritage, is more apparent than ever (McManamon 1991, 121). Conducting research on a collection such as this that has such deep ties to the community is a step in the right direction for the reintegration of archaeological research into museums.

The journal that would best fit my research is Ontario Archaeology. This peer-reviewed journal, published by The Ontario Archaeological Society, focuses on continued archaeological investigation in Ontario. As the research presented in the next chapter centers around artifacts collected in Waterloo region, it is an ideal outlet. Moreover, a majority of the chert sources are also located in Ontario as only two exotic cherts were analyzed. As the work done with XRF increases, it is important that all regions where the device can be utilized have such exploratory studies conducted.
Chapter 2

Introduction

It is understood that humans or human-like hominins were making and using lithic tools before they were using fire, yet lithics are often overlooked, even by some archaeologists, as they lack the prestige that other types of artifacts, such as ceramics, attract (Andrefsky 1998, 41; Fox 2009, 353). These artifacts once encompassed all aspects of life for the most ancient of our ancestors and they deserve archaeologists’ attention. The focus of my research centers around the chemical characterization of 32 chert artifacts from the Archaic and Woodland periods housed in the Waterloo Region Museum. They are then compared against source samples from a variety of chert outcrops and quarries throughout Ontario and its surrounding regions, with the goal being the sourcing of the artifacts to their raw material. There were ten different raw materials (cherts) included in this study (Onondaga, Kettle Point, Collingwood, Ancaster, Colborne, Haldimand, Selkirk, Upper Mercer, Saugeen, and Flint Ridge). The benefit of such research is the identification of the raw material sources to formulate greater theories about past trade, social interaction, and cultural change among Indigenous groups (Luedtke 1978).

We know that high-end portable x-ray fluorescence (PXRF) devices are capable of this type of geochemical chert analysis given the results of numerous studies (e.g., Mehta et al. 2017, Shackley 2011). However, this study makes use of a more compact PXRF than what has typically been used for these endeavors. The introduction of portable X-ray florescence (PXRF) to the field of archaeology has been plagued with controversy (Shackley 2010). The technology is rapidly advancing and is often used with minimal knowledge of its limitations (Potts 2008; Shackley 2010, 2011). The device used here – an Olympus Vanta – has a maximum voltage of 50kv, which limits its elemental range of detection.

While currently much of the work being done with x-ray fluorescence (XRF) in archaeology is used to address questions of a positivistic or processual nature, that need not always be the case. As Lothrop et al. (2018) have shown, XRF can be used as a tool to reach questions of a more qualitative or interpretive nature. In their research, they utilized XRF not as the main methodology but rather as a steppingstone to a more robust understanding of how past Indigenous groups may have utilized the landscape. The groundwork must be laid first, however, as these more involved theoretical questions require a greater understanding of which lithic sources were used and by whom. However, once this is established, archaeologists will then be able to make more complex connections. Questions of adaptation, cultural change, and the development of economies can be asked once an understanding of sources has been established (Luedtke 1978, 414). How did they get this exotic material? What other cultural groups may they have interacted with? Or were certain materials chosen out of aesthetic preference (Fox 2009, 362)? The potential questions are only limited by what we have yet to learn.

In this thesis, I will discuss the use of an Olympus Vanta and the potential limitations this and other lower voltage XRF devices carry when it comes to sourcing studies. I will do this through the comparison of the geochemical and statistical classification of artifacts to the macroscopic identification of artifacts. In this way, I will be determining potential sources for the artifacts as well. Macroscopic analysis is one of the most common methods of chert identification because it requires no instrumentation other than your own eyes (Eley and von Bitter 1989, 3). The comparison of the most common method of chert material identification with one of the newer and ever-growing methods can illustrate the faults and benefits of both. This thesis will serve as a case study for this type of research using southern Ontario materials.
Background

As they resist decay, lithic tools are the most numerous artifacts we can use to understand prehistoric lifeways (Andrefsky 1998, 1). The artifacts of this study date from the Archaic period (ca. 10,000 BP to around 2,900 BP) to the end of the Middle Woodland period (ca. 1,300 BP) (Ellis et al. 1990; Ferris and Spence 1995). The Archaic period in southern Ontario is characterized by a shift in settlement-subistence patterns over earlier times involving longer occupations at sites and resulting in more woodworking and food processing tools (Ellis et al. 1990). In contrast, the end of the Archaic period is marked by the appearance of in some cases larger and more established settlements, along with the development of ceramics. Ceramics, owing to their bulky and fragile nature, are not suited to mobile lifestyles, so they were not utilized in earnest until the Woodland period when people became more sedentary (Ellis et al. 1990; Ferris and Spence 1995; Shott 1999). A table with the projectile point types and time periods for each of the artifacts included in this study can be found in Appendix B.

As noted above, this study will focus on lithics, and more specifically, chert artifacts. Cherts are defined as sedimentary microcrystalline and cryptocrystalline silicate materials and are sometimes known as flint, jasper, hornstone, agate, and chalcedony (Luedtke 1978, 414). Geologists may refer to chert as microcrystalline quartz, however, chalcedony is a fibrous form of quartz (Andrefsky 1998, 54). These terms refer to the method of formation of the material and have no effect on its chemical composition (Andrefsky 1998, 54). In southern Ontario, cherts are thought to have formed in deep-sea environments during the Ordovician, Silurian, and Devonian periods due to their high silica content, which is caused by the decay of silica-secreting organisms like diatoms (Andrefsky 1998, 54; Eley and von Bitter 1989, 1).

One of the more prominent issues with the study of southern Ontario cherts is that geological literature is limited as there are no major modern uses for chert (Fox 2009, 354). This disconnect between archaeologists and geologists is further worsened by our lack of consistent terminology for sources (Andrefsky 1998, 41). For a majority of humanity’s past, the recognition of suitable stone for tool making would have been learned at a young age, but since so few modern technologies incorporate rock, much of this skill has been lost (Andrefsky 1998, 41). This means that there still may be chert sources that would have been exploited by prehistoric peoples that are not known by archaeologists today. Moreover, the lithic materials found throughout Canada are highly varied (Reimer 2018, 137). These factors combined can make the collection of source samples difficult, and practically impossible to analyze samples from every possible source in southern Ontario. This issue is made worse by the addition of exotic materials that may have been brought in from other regions during the last Ice Age. In southern Ontario, one of the most commonly used cherts is Onondaga which appears in glacial deposits, but also outcrops in bedding planes along the northeastern shore of Lake Erie. This chert is high quality and varieties can also be found on or near the surface, notably in the Decewsville area near Cayuga, so it was often used by past Indigenous peoples (Fox 2009). There can be much difficulty, then, in determining the exact location of its various manifestations.

Despite these challenges, one of the goals of this study is to source chert artifacts by geochemically matching them to their geologic formation. The term ‘source’ is used to refer to the location that the chert was originally obtained from as a raw material (Luedtke 1979). According to Shackley (2008) sourcing is one of the most poorly characterized terms in archaeology. To put it simply, chert and other lithic materials cannot be truly assigned to a source. Instead, archaeologists are stating that it is statistically probable that an artifact originates from a particular source (Luedtke 1979; Shackley 2008). It is this definition of sourcing that will be used throughout this study. It should also be considered that chert is one of the more difficult materials to source as it can be found across a large
geographic area and, as a result, has a high degree of isotopic and elemental variability (Shackley 2008). In the case of my research, Onondaga chert would be an excellent example of this phenomenon. Due to this variability, the chemical characterization of chert lags behind studies of other more homogenous stones such as obsidian and marble (Shackley 2008). Despite the high degree of internal variation within sources, there is still more variation between sources (Luedtke 1979). A majority of chert is composed of silicon dioxide (SiO2) so it is in the trace elements where the most distinctive variation between sources can be found (Luedtke 1979). In addition, archaeologists can only link artifacts to sources that have been or will be analyzed in the same way (Reimer 2018, 140), a limiting factor that should always be addressed in studies.

Before the advent of chemical characterization, chert could only be identified by its macroscopic properties (see Biittner and Jamieson 2006; Eley and von Bitter 1989). Here, chert types are identified by traits that can be seen with the naked eye such as color and texture. This method typically works best with larger samples so more visual traits can be observed. Petrographic analysis, on the other hand, refers to a sample’s mineral composition as seen through a microscope (Biittner and Jamieson 2006, 16-17; Eley and von Bitter 1989). This often involves the cutting of a sample into thin slices, so it is a destructive method. Another method, palynological analysis, involves the analysis of a sample’s microfossils that can be seen when an acid is applied to break down non-fossil materials (Biittner and Jamieson 2006, 17-18; Eley and von Bitter 1989). While the acid is not always needed to reveal the fossils in a chert, palynological analysis can often be destructive. While these visual identification methods, especially macroscopic identification, can be cost effective and quicker than chemical analysis, they have a high error rate. This is because for many sources, chert is more chemically than visually distinct (Luedtke 1979). It is also important to know that coloration in chert is not correlated with its elemental components in a simple and straightforward manner, even within chert types (Luedtke 1978, 416). This means that many cherts can display a wide variety of colors while will still having similar chemical compositions. This is why provenience studies of lithic sources are best performed using geochemical methods (Andrefsky 1998, 59).

There are many methods for measuring the chemical compositions of cherts, such as Neutron Activation Analysis (NAA) or Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). This study makes use of X-ray fluorescence (XRF) which allows users to detect and measure the elemental composition of substances by exciting atoms to fluoresce by use of x-ray beams. It carries with it many analytical advantages, including: 1) it is non-destructive, 2) only minimal preparation of the sample is needed, 3) it takes an average of 5-6 minutes to analyze each sample, 4) it is relatively easy to use, and 5) it is relatively cost effective compared to other methods for measuring chemical composition (see Shackley 2011, 8-9). The first archaeologist to make use of this technology was Edward Hall (1960) when he published a paper discussing the validity of the method. Many of his assertions have changed very little despite 60 years having passed (Shackley 2011, 1). One of the earliest uses of XRF in Canada came not long after Hall’s work. In the early 1970s, Erle Nelson and John D’Auria of Simon Fraser University built an XRF spectrometer with the goal of sourcing obsidian in the Pacific Northwest (Reimer 2018, 139). Essentially, modern XRF devices emit an X-Ray laser beam from an aperture that contacts the targeted material causing the atoms of the material to fluoresce (Shackley 2011, 16). When an atom is excited in this way, an electron on an inner shell is dislodged and replaced by an electron on an outer shell which produces its own secondary or fluorescent X-Rays (Andrefsky 1998, 44; Shackley 2010, 17).

While it is theoretically possible to measure almost all the elements in a periodic table with XRF, most devices are better suited to low-energy elements and silicon is often the highest element that can be accurately measured (Potts 2008, 4). To measure silicon and other higher elements one must use
helium, so the air does not affect the results (Shackley 2011, 16). The data gathered from this process is turned into what is known as spectra, and it is from these spectra that conclusions can be reached (Drake 2016). The locations of the peaks on the spectra indicate which elements are present while their heights represent how much of the element is present (Andrefsky 1998, 44; Drake 2016; Shackley 2011). It is important to note that the comparison of elements within a sample is not practical as the method is designed to detect the same elements in multiple samples (Shugar 2013). It is vital to keep this limitation in mind when a study that is planning on using XRF is developed.

The most recent development in XRF is the now widespread use of portable x-ray fluorescence (PXRF). The emergence of portable XRF devices was quick and overwhelming to many researchers in the early 2000s (Shackley 2010, 17). PXRF’s greatest benefit is that it can be used when conventional sampling is not possible or practical (Potts 2008). PXRF can be used in situ, which in this context means the instrument can be taken directly to artifacts or potential source outcrops. This means that artifacts that are too large or too valuable to move can be easily analyzed. An additional benefit of PXRF is that the results are immediately available to the operator (Potts 2008). Some publications will refer to PXRF as handheld XRF (HHXRF) although it is not very common with more recent studies (Shugar 2013). The development of PXRF as a method has been rapid in the past decade due to advances in miniaturization and semiconductor detector technology, but the most important development is the ability to create miniature x-ray tubes (Potts 2008). Due to the compact size of PXRF, in comparison to Energy Dispersive X-ray Fluorescence (EDXRF), these devices have a smaller power source which results in a weaker x-ray (Shackley 2011). Moreover, as a result of its miniaturization, PXRF has a larger error rate than traditional EDXRF (Shackley 2011). Despite this higher error rate, the chert sources are most often chemically distinct enough to still be distinguishable. One of the more prominent issues with this new advancement is the lack of analytical rigor applied to PXRF in comparison to lab-based instrumentation like EDXRF (Shackley 2008). For data produced by PXRF to be considered valid, it must be held to the same strict protocols as other XRF devices (Goodale 2012; Shackley 2010).

Methodology

For this study, arrangements were made with Stacy McLennan, Collections Curator and Registrar with the Waterloo Region Museum, to analyze 32 artifacts from their permanent collections. The artifacts were selected using stratified random sampling. This sampling method was selected to ensure that the artifacts were representative of the collection. As noted in Chapter 1, these artifacts were donated by Nathaniel Stroh in 1952 but had been collected by his father Jacob Stroh in the late 1800s and early 1900s, likely from Waterloo region. While it would have been ideal to test more artifacts in this collection, this was considered impractical due to time constraints. The artifacts used in this study are labeled by the last few digits of their accession numbers. Since they are all a part of the same collection, the artifacts all share the same initial numbers (i.e., 57.53.1).

The tool stones were all visually identified by their macroscopic features with the help of Mr. William Fox, whose work with chert sourcing in Ontario and adjacent areas is extensive (see e.g., Fox 2009). These visual identifications were intended to act both as a comparative “control” to the geochemical identifications and as a basis with which to judge the accuracy of the XRF and my statistical analysis. These identifications further aided in the process by limiting potential source samples. Due to the time constraints of the study, it was decided not to measure all the potential sources that could be found in southern Ontario and instead limit the sources under examination to the ones likely for these 32 artifacts. This means the sources that were selected for this study had similar visual characteristics.
(e.g., color and luster) to the artifacts. While in an ideal world all sources that can be found in the region would be assessed, this is not practical.

As for the sampling of the raw materials, certain allowances were taken owing to time restrictions with the XRF device. Three readings were obtained from each of 56 source samples for a total of 168 readings. Sources were provided principally by Mr. William Fox, who very graciously made his wide-ranging collection of chert samples available to me for the purposes of this study. Additional samples of Onondaga chert were obtained from Mr. Chris Dalton, a local avocational archaeologist and flintknapper, and from samples on hand in Dr. Chris Watts’s lab at the University of Waterloo that are typically used for visual identification. Collectively, this resulted in 24 Onondaga chert samples, three Upper Mercer chert samples, two Saugeen chert samples, six Kettle Point chert samples, four Haldimand chert samples, seven Collingwood chert samples, two Colborne chert samples, one Ancaster chert sample, and two Selkirk chert samples.

Notably, Onondaga was the most sampled chert type for several reasons. First, it is one of the most commonly occurring tool stones in Southern Ontario due to the many locations where it is found. This, however, also means that it has a large amount of internal variation. Secondly, it was also by far the most visually identified chert type in the artifact assemblage. Figure 1 depicts the location of origin for the chert source samples used in this study as well as where Gordon Lake chert can be found. We were unable to obtain a source sample of Gordon Lake chert for this study, but one of the artifacts has been visually identified as this material. The figure also marks the location of the Region of Waterloo, where the artifacts were found. These are not the only locations these chert types can be found but, with the exception of the Gordon Lake markers, this is where the samples originate. For example, Onondaga chert can be found in the state of New York as well. The majority of the chert sources analyzed are from southern Ontario with the exception of Upper Mercer chert and Flint Ridge chert which are both from Ohio.

Fig. 1. Location of the Region of Waterloo in relation to the chert sources analyzed in this study. The source markers are reflective of the source samples included in this study with the exception of the Gordon Lake markers, which are approximate in the absence of study samples.
Additionally, it is important to note that some of the cherts mentioned above have alternate names. Kettle Point chert is also referred to as Port Franks chert while Selkirk is also known as Dundee Formation chert (Eley and von Bitter 1989, 15-16). Saugeen, Colborne, and Haldimand all come from the Bois Blanc Formation (Eley and von Bitter 1989, 18) while Collingwood is also known as Fossil Hill Formation (Eley and von Bitter 1989, 18, 22). As well, Ancaster is also known as Lockport Formation or Goat Island Member chert (Eley and von Bitter 1989, 19) while Flint Ridge is a type of chalcedony that formed in VanPort limestone, so it is sometimes referred to by those names (Reber et al. 2017, 248). Upper Mercer is also known as Coshocton and Nellie Chert (Reber et al. 2017, 257).

PXRF was selected as the mode of geochemical evaluation due to the speed and ease of the instrumentation, not to mention the cost benefits to the method. For this study, I was able to use an Olympus Vanta C Series (VCA) PXRF with a silver anode X-ray tube, which was on loan to the Department of Anthropology from the manufacturer. This device is known to produce precise readings for a portable XRF provided it is adequately calibrated. Goodale et al. (2012) showed that the while Olympus PXRF devices' preset calibrations are not as precise as a lab-based model, they are adequate for a study such as this. The mode that was used during the analysis was the Geochem (3-Beam). In this mode, the first beam runs at 40 kilovolts (kv) for 20 seconds (s) and targets a wide range of elements (i.e., Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Nb, Sn, Ba, W, Hg, Pb, Bi, Th, U, and LE). The second beam runs at 10kv for 40s and targets lighter Elements (i.e., Mg, Al, Si, P, S, Cl, Ca, Ti, and Mn). The final beam runs at the device’s maximum voltage at 50kv for 120s and targets heavier elements (i.e., Ag, Cd, Sn, Sb, Ba, La, Ce, Pr, Nd, and LE). The abbreviation LE stands for light elements which are more difficult to detect using this device. The Olympus programing combines several of these lighter elements (Mg, Al, Si, P, S, Cl, K, and Ca) into one measurement which it refers to as LE. The default time setting for the Geochem (3-Beam) mode is 90s. In an effort to obtain more distinct measurements, I doubled this run time to a total of 180s. Shackley (2011) recommends a run time of 100 to 200s for this kind of analysis so my run time of 180s fits comfortably within this range. Unfortunately, we were unable to acquire a stand for the device so each of the three-minute readings had to be undertaken with a still hand. While not unheard of, this is not an ideal method. Lastly, the device was only in my possession for two weeks which caused some of the time constraints seen throughout the study.

When analyzing the data obtained from the XRF, I looked to past studies to see which elements are the most distinctive. There are several minor elements (P, Ca, K, and Cl) and trace elements (Ti, V, Cr, Bi, Th, M, Sr, Pb, Zn, Zr, Cu, Fe, Ni, and Y) that can be distinctive for certain chert sources (Mehta et al. 2017, 384). As previously stated, the major elements are not particularly distinctive. While I used these elements as a guide, I found some to be not as useful with the lower voltage output of the PXRF used in this study. The elements I found most useful for creating distinct groups of chert sources were ultimately much shorter than the ones listed above (i.e., Al, Si, P, S, Cl, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Y, Zr, and Mo). These elements were determined to be most helpful through some statistical analysis. Some elements were not detected in a high enough quantity to be analyzed as their parts per million (PPM) were under the level of determination (LOD). Other elements were determined by preliminary discriminant analysis not to be particularly variable between the sources included in the study. Finally, some elements had numerous outlier readings among chert types or even among multiple readings of the same samples. This was determined by creating distribution graphs for each element of each source in the Statistical Package for Social Science (SPSS). The elements with high outliers were determined to be unreliable and were excluded.

Very little was needed in the way of sample preparation. Since XRF partially penetrates the artifact, according to Shackley (2011) dirt can be left in the crevices and still produce valid data. Owing
to their lengthy curatorial stay at the Waterloo Region Museum, the artifacts examined in this study were all clean, as were the source samples.

To perform the statistical analysis of my source samples and artifacts, I employed SPSS. This program has been in use for decades and has proven to be reliable (Luedtke 1979). Using this program, I performed discriminate analysis on the source samples. The independent variables were entered together rather than in a stepwise method and the data were computed from the group size as the number of samples taken from each source varied. Discriminant analysis is considered a good method of categorizing the chert types as it gives weight to the minor and trace elements (Luedtke 1979). Jarvis (1990) also employed this form of statistical analysis in their chemical characterization of Onondaga chert. Discriminant analysis is a statistical method that sorts categories using given data. In this case, it sorts the artifacts into chert types given the amounts of each element present. Results were then provided with a confidence interval in the form of a score between 1 and 0. These scores were achieved by the probabilities of group membership function of SPSS.

Results

Table 1 shows the classifications for each of the artifacts according to both the visual and statistical geochemical identification methods. This table also features the confidence interval, which is a measure of SPSS’s certainty that the artifact belongs to that classification with 1 being complete certainty and 0 being a non-classification. Table 2 shows the rate of correct classifications when the source samples are run through the same formula that was used to classify the artifacts. Using this table, one can assess how accurate the classifications are for each chert type as well as the overall accuracy of the formula. Table 2 shows a 79.9 percent success rate of classification of the chert source samples and a 71.6 percent success rate when cross validated. Figure 2 shows the distribution of the chert sources as well as how the artifacts are distributed. In Figure 2, the artifacts are referred to as the ungrouped cases.

All of the artifacts visually identified as a type of Onondaga chert were classified as Onondaga in my geochemical analysis. However, only one artifact that was not visually identified as Onondaga had a corresponding identification with the geochemical, statistical analysis. The artifact in question (artifact 99) was both visually and geochemically identified as Kettle Point chert. To determine how many “matches” there were between the visual identification and the geochemical identification there are some exclusions to consider. The artifacts that could not be visually identified and the one artifact that we were unable to procure a source sample for (artifact 95) need to be excluded from this statistic. This leaves 25 visually identified artifacts with which we can compare the discriminant analysis classifications. Of these artifacts, 19 had matching visual and geochemical identifications. This is an accuracy of 76 percent which exceeds the success rate of the cross validated cases determined by SPSS.

At this point, it is important to address the types of errors that can develop with data of this nature. Luedtke (1979) describes three types of errors that can occur when using discriminant analysis to source chert. A type 1 error is the classification of an artifact as a variety of chert when the real material source is another chert in the study. This is likely the case for a few of the artifacts in this study, and this is where the classification success rate of SPSS comes into play. Of the chert sources, 79.9 percent of original grouped cases were correctly classified, while the same could be said of 71.6 percent of cross-validated grouped cases. This means that while the classificatory exercise can be considered statistically significant, there remains a notable amount of source material that was incorrectly classified. There is a noteworthy chance of the artifacts being misclassified as another type
<table>
<thead>
<tr>
<th>Accession Number</th>
<th>Visual Identification</th>
<th>Discriminant Analysis Identification</th>
<th>Confidence Interval</th>
</tr>
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<td>Onondaga</td>
<td>0.52436</td>
</tr>
<tr>
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</tr>
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<td>Kettle Point</td>
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</tr>
<tr>
<td>225</td>
<td>Kettle Point</td>
<td>Onondaga</td>
<td>0.49904</td>
</tr>
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</table>

Table 1. Comparison of visual and discriminant analysis identifications using the data produced via the Olympus Vanta XRF for each of the artifacts. The confidence interval of the discriminant analysis classification is listed for each artifact.
Table 2. Predicted Group Membership for source samples when classified using the same discriminant analysis formula with which the artifacts were classified.
of chert within the study. As depicted in Figure 1, many of the chert source samples are clustered together quite tightly. As noted in figure 2, Ancaster chert is particularly distinct from the other chert types and therefore the least likely chert to be subject to this kind of error.

A type 2 error occurs when a chert is determined not to be a type that is in the study when it is in fact present. This happens when a researcher determines the confidence interval is too low for the chert to be a match to the source materials in the study. Any artifact with a confidence interval lower than .75 should be examined for accuracy and anything lower .5 should be critically examined. In this study, there are three artifacts that have confidence intervals lower than .5 (artifacts 46, 90, and 225). Closer examination of these artifacts is needed to determine whether they are a match to the material sources in the study.

A type 3 error arises when an artifact is identified as a chert within the study, but that chert is not included. This is, unfortunately, not totally unavoidable as there will always be more chert types out there than one can reasonably include in any given study. This is especially important as there are many possible chert sources that archaeologists are not aware of yet. An example of this type of error appears with artifact 95 as I was unable to obtain a sample of its visually identified source. The artifact was visually identified as Gordon Lake chert and the discriminate analysis identified it as Saugeen. In fact, it had the most affirming confidence interval possible with a score of 1. However, the material is clearly not Saugeen, which is a white and grey material, and the artifact has the green appearance of Gordon Lake (Fox 2009, 358). The Gordon Lake formation has rough jasper rather than quality chert (Chandler 1988). It is this description that the artifact more closely resembles.
Taking this into account, let us discuss the artifacts that were not visually identified. Many of these unidentified artifacts are rather small, which makes visual identification more difficult as there is less surface area for characteristics of the chert to manifest. To start, artifact 11 was classified as Haldimand chert using discriminant analysis with a high confidence interval (0.93258). The artifact does bear a resemblance to this chert type as its appearance is grey blue with white inclusions and the porcelaneous luster associated with Haldimand (Eley and von Bitter 1989, 19). Artifact 46 was also identified as Haldimand by discriminant analysis but with a very low confidence interval (0.47507). However, this artifact does not have the visual characteristics of Haldimand. The visual characteristics of the artifact look to match Onondaga more than Haldimand as it has a brown and tan mottled appearance (Eley and von Bitter 1989, 17). The combination of these factors would suggest a type 1 error. That said, since all the artifacts visually identified as Onondaga were statistically classified as Onondaga, there may be more at play in this case.

Artifact 49 was identified as Saugeen chert with a high confidence interval (0.95359). It has the grey coloration and porcelaneous luster of Saugeen, so this classification is plausible (Eley and von Bitter 1989, 19). Artifact 55 was identified as Collingwood with a middling confidence interval (0.75378). While the confidence interval is somewhat low, the artifact does have the white coloration with the “salt and pepper” speckles and the earthy to dull luster one can expect from Collingwood chert, so this classification is also plausible (Eley and von Bitter 1989, 22). Artifact 114 was identified as Onondaga with a mediocre confidence interval (0.70775). This artifact does not resemble the visual characteristics of Onondaga and is likely an example of a type 3 error. The artifact has banded stripes of a darker brown grey that run through its otherwise grey appearance. These characteristics are not associated with Onondaga or any of the other chert sources included in this study. Artifact 191 is a particularly interesting case as it appears to have been heat-treated. It has the distinctive scarlet coloration of heat-treated chert which can obscure the visual identifiers. Discriminant analysis identified the chert as Saugeen chert with a high confidence interval (0.99209). The artifact has a coloration that may have been a white or light brown before the heat treatment which corresponds to Saugeen chert (Eley and von Bitter 1989, 19). However, the artifact has a somewhat dull luster for Saugeen which has a porcelaneous to vitreous luster (Eley and von Bitter 1989, 19). This would not be something affected by heat treating as, if anything, the process of heat treating can increase luster (Collins and Fenwick 1974, 137). Despite this, it would appear to be a plausible identification.

It is also important to discuss the artifacts that were not geochemically matched to the same chert with which they were visually identified. As previously mentioned, all the artifacts that were visually identified as Onondaga had corresponding geochemical identifications. This means that all the artifacts that were not attributed to the same source were made on other cherts. Artifact 90 was visually identified as Flint Ridge, but it was geochemically matched to Collingwood albeit with a very low confidence (0.49677). While the white coloration of the artifact is found in both Flint Ridge and Collingwood chert, Collingwood chert has a wide range of lusters but none that match the waxy luster of Flint Ridge (Eley and von Bitter 1989, 22; Rebber et al. 2017, 248). The artifact has a waxy appearance and therefore may be an example of a type 1 error. Artifact 119 was visually identified as Upper Mercer, but it was geochemically matched to Onondaga with a low confidence interval (0.55811). It has the black coloration and the waxy luster that is common for Upper Mercer (Rebber et al. 2017, 257). This may be another example of a type 1 error. Both artifact 90 and artifact 119 were visually identified as chert types that come from Ohio and would therefore be considered exotic. Interestingly, they also both seem to be the same type of projectile point (i.e., Snyders). This type of point dates to the Middle Woodland and can be found in both Ohio and southern Ontario (Justice 1987, 201-204).
Artifact 177 was visually identified as Collingwood chert but geochemically identified as Flint Ridge with a high confidence interval (0.84858). The artifact has the visual appearance of Collingwood as it is white with “salt and pepper” speckling that has oxidized to a rust color and a red staining that sometimes occurs. The artifact also features the dull vitreous luster that can occur in Collingwood chert (Eley and von Bitter 1989, 22). This is likely a type 1 error. Artifacts 181 and 225 were visually identified as the maroon presentation of Kettle Point chert and both were geochemically identified as Onondaga with low confidence intervals (0.50387 and 0.49904). These artifacts are particularly difficult to visually identify as the maroon to brown color is very similar to Onondaga as well. These artifacts could be correctly geochemically classified, or it could be a case of a type 1 error due to under sampling of the source material. Artifact 210 is visually a textbook example of Kettle Point chert, but it was identified as Onondaga with a modest confidence interval (0.75385). It has the blueish grey coloration with white mottling and the waxy luster that is characteristic of Kettle Point chert (Eley and von Bitter 1989, 15). Again, this is potentially an example of under sampling and very likely an example of a type 1 error.

Discussion

Taking the results of the geochemical and statistical analyses into account, there is an unavoidable fact that presents itself. It is only through the culmination of both the data produced with the XRF and visual identification that this methodology can be employed. Comparing the discriminant analysis classifications to the visual identifications allows researchers to identify faults in their study. In this way, the visual identifications act as a sort of control group with which one can compare the geochemical analysis. It is only the conjunction of the two methods that makes the data produced from this study useful. Basic visual identification can be used as a starting point for the initial sorting of materials (Reimer 2018, 139); however, macroscopic analysis will never be an adequate means of chert sourcing alone (Bittner and Jamieson 2006, 25). This may not be the case for all studies of this nature but given the low voltage output of the PXRF employed, it is certainly the case here. Those who think of XRF as some sort of magic laser that can miraculously tell the user the source of a material need to consider the real limitations of a device like this (Reimer 2018, 140). The findings will never be 100 percent certain so using other methods to guide the process will often be necessary. Visual identification has remained a critical skill in chert sourcing despite the commonplace use of geochemical methods of the past decades for a reason.

Taking this into account, there are several factors that should be considered when examining data produced with the XRF and statistical analysis. To begin, the low voltage of the Olympus Vanta meant that elements that are often used for chert sourcing went undetected in my samples or were detected intermittently and unreliably. The more elements that are included in a discriminant analysis, the higher the percentage of cross validated source samples (Luedtke 1979). If more elements were to have been included in a study such as this, there likely would be fewer misclassified artifacts. In addition, the use of the device as a handheld instrument without the use of a stand can make for less reliable data. This may be the cause of the outliers discussed in the methods section. Had the device been held perfectly still with the aid of a stand, perhaps more elements could have been included in the statistical analysis.

An additional factor to consider in this study is the under sampling of the chert sources. Had I been able to spend more time with the XRF device, I may have been able to analyze additional sources. In the future, I would aim to develop a more complete depiction of the elemental variation within the sources. One sample is not considered enough to properly chemically characterize an entire source
(Luedtke 1978). To properly sample a small chert source, at least 30 samples should be taken while hundreds of samples may be needed for larger sources (Reimer 2018). Approximately five samples should be taken from each outcrop and the location of the samples should be recorded in some manner such as GPS (Shackley 2008). The larger the sample size, the more accurate the chemical characterization of the source (Luedtke 1979). This is, of course, quite the undertaking, and one beyond the scope of the present study and its time constraints. The source samples in this study were not obtained from the field but rather extant collections, the characters of which do not necessarily lend themselves well to this type of work.

This point is thrown into sharp relief by the maroon variant of Kettle Point chert. Of the artifacts I examined, there were two that were macroscopically identified as this type of Kettle Point chert, but neither of the artifacts were statistically matched to it. I was only able to analyze one maroon Kettle Point chert sample with the PXRF which, sadly, provides very little data to confidently state whether these two artifacts were or were not made on this variety of Kettle Point chert. Only one artifact that was not visually identified as Onondaga had a matching geochemical identification. Onondaga was by far my most sampled source, so it follows that it was my most accurate chert type to source. When a certain group makes up a majority of the population of samples and of the group being classified, there is a significant likelihood of it being correctly classified by chance when one uses discriminant analysis (Morrison 1969). If all the other sources had been as numerously sampled, there would likely have been a higher degree of accuracy for them as well.

Interestingly, there is also some evidence that archaeologists may be able to differentiate between outcrops within one geologic formation (Luedtke 1978, 420-422). This hypothesis is further explored using XRF by Sánchez de la Torre et al. (2017) where they observed that the Castelltallat formation in the Central-Eastern Pre-Pyrenean area in southwestern Europe was large and internally varied enough that the researchers were able to distinguish between outcrops. Similar work was done with Carson Mounds in Mississippi where researchers were able to geochemically categorize different sources of Burlington chert (Mehta et al. 2017). This provides a very intriguing new research avenue for the chemical characterization of chert, especially Onondaga as there are so many sources of it that can vary greatly in visual characteristics. It would be very interesting to see if this visual variation corresponds with geochemical variation. While I previously stated that visual variation is very complexly related to chemical variation, that does not fully discount the connection. Further examination of this possibility of formational variation of Onondaga is particularly interesting since the chert has been moved via the processes of glaciation. A study by Jarvis (1990) has already made some headway in this query using NAA but the issue warrants further examination. This would also be a possible avenue of exploration for the three Bois Blanc Formation cherts (Haldimand, Saugeen, and Colborne). Further examination of the geochemical differences of these cherts that share a formation may help in further distinguishing the three. With a greater variety of source samples, questions like this can begin to be answered. The statistical analysis also fails to account for the proximity of the various chert types to Waterloo region. When high quality chert, such as Onondaga, is abundant, then many formal and informal tools can be made from the material (Andrefsky 1994). The fact that a majority of the chert types identified in this study are found in southern Ontario is to be expected. The more exotic cherts from Ohio (Upper Mercer and Flint Ridge) and to an extent Gordon Lake chert from north of Lake Huron are much less common in southern Ontario. For much of the Archaic and Woodland periods, southern Ontario was on the peripheries of many trade and exchange networks in eastern North America (Ferris and Spence 1995, 101-102). This means that while the chance of identifying exotic materials here is low, it is certainly not unheard of. The two Snyders type projectile points made of exotic Ohio materials are outliers from my assemblage, but they are not wholly unique. There is evidence that Snyders points
made of exotic material may have been used for display pieces (Fox 2010). This suggests that there may
have been some sort of status associated with having these sorts of exotic cherts at this time.

There are other factors that may affect the geochemical results that are not the fault of the
researcher. Artifacts may be leached or stained by the soil matrices in which they reside, which can
change the elemental composition of the material (Luedtke 1978, 419). The artifacts may have also
been further contaminated by their time in Jacob Stroh’s possession or even during their time in the
museum. Since XRF measures elements near the surface of the material, it is easy for the readings to be
affected by contamination. As soon as an artifact is removed from its source it begins a process that can
change its elemental composition. That said, there is not much to suggest that the results of this
process are dramatic enough to make the artifact geochemically indistinguishable from its source.

Considering all of this, the number of plausible geochemical identifications made for the
unknown artifacts is rather encouraging for a study of this nature. Four of the six unknown artifacts
returned plausible identifications, which is good considering the issues mentioned above and the
misclassifications for the visually identified artifacts. This is also why artifact 191 is the most notable of
the unknown artifacts in this study. Since it seems to have been possibly heat-treated, it was hard to
identify with visual methods alone. The rosy coloration caused by the heat-treating process has the
potential to obscure visual markers that can be vital to its identification. As there are many lower
quality cherts in the region with white coloration, it is significant that the geochemical analysis was able
to give us more insight into its possible source. It is also unlikely that this artifact came from outside this
region; if chert looks to be of poor quality, it likely did not travel far (Fox 2009, 364). It is the existence
of artifacts such as these, made of unidentifiable chert, that gives rise to the importance of geochemical
analysis. Artifacts that are too small or cherts that are too similar are prime examples of why visual
identification is simply not enough.

Ultimately, the data produced in the course of this study is useful despite the limitations
described above. The many artifacts examined here with plausible identifications are a testament to XRF
and its capabilities. With a little guidance from the macroscopic visual identification, and the assistance
of others, I was able to confidently attribute artifacts to sources.

**Conclusions**

The importance of filling in any gaps in our understanding of the past cannot be understated.
Since the prevalence of PXRF is continuing to rise in archaeology, it is necessary to highlight the types of
studies to which this form of instrumentation can be applied. In this study, I have done just that by
utilizing the Olympus Vanta PXRF and testing it under circumstances that would be considered not ideal.
For example, there was no stand to hold the device steady and the variety of chert samples was limited.
The methodology used is consistent with many similar studies. Moreover, discriminant analysis proved
to be a valid method of statistical analysis and the classification for geochemical chert sourcing just as
Luedtke (1979) suggested. It is clear that under sampling of the various chert sources is one of the more
limiting factors that has affected the statistical analysis of this study. The range of elemental variation
within the sources was not fully captured which inherently limits the classification of the artifacts. In
future research in this region, more thorough sampling would of course need to be conducted. This
process, ideally, would involve going into the field and systematically collecting chert source samples.

While the limitations of my study are evident, the results are rather promising. I firmly believe
that if more source samples had been analyzed the results of the study would be more affirming of PXRF
as a methodology. That said, PXRF as a technology should not stand alone. It is rather a tool to be used alongside the more established forms of chert identification such as macroscopic identification. Both methods alone are flawed but, when combined, these flaws can be greatly reduced. There will likely never be a method that is wholly without misclassifications so all we can do is limit them as often as we can. Ultimately, PXRF is still emerging as a methodology in archaeology and the technology is rapidly changing (Shackley 2010, 18). The effects that it will have on archaeology are still not known. Its accessibility to a wider group of people will have both positive and negative effects as not everyone will be as cautious with their sourcing claims as I have been. The best way forward is to continue to rigorously test the new technology developed. Rushing to implement a method like this with those who are not well versed in the technology and its principles need to understand the data produced could be flawed. However, the future is not bleak as there are many archaeologists who seem to be taking on this challenge and producing excellent work. I look forward to seeing how the methodology progresses.


Mehta, Jayur Madhusudan, Grant McCall, Theodore Marks, and James Enloe (2017).


## Appendix A: XRF Data

| AO | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V |
| 0 | 5 | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |

### Notes
- The data in this table represent measurements taken using X-ray fluorescence (XRF) spectroscopy.
- Columns A to T contain raw XRF counts at various photon energies.
- Columns U to Z are derived parameters based on the raw counts, such as elemental abundances or other analytical results.
Raw elemental Composition data for all the source samples and artifacts. SPSS classifications for chert types and confidence intervals for each of the chert types.
Appendix B: Artifact Typology and Dating

<table>
<thead>
<tr>
<th>Accession #</th>
<th>Point Type ID</th>
<th>Temporal Range</th>
<th>Period Identifier</th>
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<tbody>
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<td>Kirk Corner Notched</td>
<td>7500-6900 BCE</td>
<td>Early Archaic</td>
</tr>
<tr>
<td>188</td>
<td>Kirk Corner Notched</td>
<td>7500-6900 BCE</td>
<td>Early Archaic</td>
</tr>
<tr>
<td>198</td>
<td>Possible Kirk Corner Notched Preform</td>
<td>7500-6900 BCE</td>
<td>Early Archaic</td>
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<td>Raddatz Side Notched</td>
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</tr>
<tr>
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<td>Raddatz Side Notched</td>
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<tr>
<td>96</td>
<td>Bottleneck Stemmed</td>
<td>3800-3000 BCE</td>
<td>Late Archaic</td>
</tr>
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<td>12</td>
<td>Brewerton Corner Notched</td>
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<td>Brewerton Side Notched</td>
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<td>Snook Kill</td>
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<td>181</td>
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<td>177</td>
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<tr>
<td>108</td>
<td>Raccoon Notched</td>
<td>500-1000 CE</td>
<td>Middle Woodland</td>
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</tbody>
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Projectile point types and time periods for each artifact included in the study.
Appendix C: Artifact Photos

Artifact 3

Artifact 11