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Preliminary Studies in Using X-Ray Diffraction for Analyzing the Atomic Structure of Central Plains Tradition Constituents

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Preliminary Studies in Using X-Ray Diffraction for Analyzing the Atomic Structure of
Central Plains Tradition Constituents

By

Zachary Day

A Thesis

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Master of Arts

Major: Anthropology

Under the Supervision of Professor LuAnn Wandsnider and Professor Matthew Douglass

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PRELIMINARY STUDIES IN USING X-RAY DIFFRACTION FOR ANALYZING THE ATOMIC STRUCTURE OF CENTRAL PLAINS TRADITION CONSTITUENTS

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University of Nebraska, 2016

Advisors: LuAnn Wandsnider & Matthew Douglass

This master's thesis is a compilation of two standalone papers, one being methodological and the other consisting of preliminary results, that are united by a common theme. These papers explore the experimentation and workflow in the design of and implementation of an X-Ray Diffraction methodology for describing the atomic structure of Central Plains tradition ceramic constituents. The devised methodology would implement new technologies available to X-Ray Diffraction equipment to create a workflow that is rapid and minimally destructive to the artifacts, but at the same time allow for extremely accurate data on the chemical composition of the clays present in the ceramics. Potentially, XRD could serve as a means for sourcing ceramics in the Central Plains tradition, which past sourcing studies have found challenging.

Acknowledgements

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CHAPTER 1: Introduction

This thesis is a compilation of two papers that discuss the development and application of an X-Ray Diffraction (XRD) methodology to assist in ceramic characterization. Current generation XRD, explored here, minimizes destructiveness to ceramic artifacts while maintaining a high level of data acquisition accuracy. I apply this developed methodology to Central Plains tradition (CPT) ceramic artifacts from McIntosh (25BW15) and Patterson (25SY31) sites, located in Nebraska and are associated with CPT populations, to investigate WHAT. The goal of this thesis is to develop, evaluate, and apply this minimally destructive, precise and accurate analytics method, to characterize ceramics. Both papers and this thesis represent a case study in a larger project to examine the movement and interaction of CPT populations in the Central Plains region. The case study shows that XRD can be a viable characterization technique in the pursuit of examining these interactions and trends via movement of clays used in the ceramic production at CPT sites.

X-Ray Diffraction is a qualitative characterization analytic technique that incorporates x-ray radiation to look at the crystal lattice and d-spacing on crystal or powder to determine the structure of the atoms and molecules. It is able to differentiate differences between structures even assuming they have the same elemental profile thus it

can detect minute differences between samples. The technique explored here incorporates this high level of detail analysis while maintaining a low level of destructiveness. It utilizes new technology available to XRD based equipment, a heatstage module, which allows for small amounts of sample to be fired and analyzed in real-time. The first paper of this thesis discusses the experimentation and development to incorporate this heatstage module into a reliable and accurate characterization protocol.

The second paper of this thesis, Chapter 3, discusses the preliminary results achieved using this new methodology on a selection of ceramic artifacts from two Central Plains tradition sites. The sampling size of ceramic artifacts is small, with twenty-six sherds from the Nebraska Sandhills site McIntosh (25BW15) and four sherds from the Nebraska Phase site, Patterson (25SY31) located in the eastern part of Nebraska. I discuss the basic implications of these results of the characterization results achieved by the heatstage XRD methodology, as well as highlight how the future of the study will proceed.

CHAPTER 2: DEVELOPMENT OF A NON-DESTRUCTIVE X-RAY DIFFRACTION METHODOLOGY FOR ATOMIC STRUCTURE ANALYSIS

Abstract:

This paper describes the development of X-Ray Diffraction as a characterization technique for ceramics. It focuses on defining aspects of the sampling and scanning protocols. Ultimately, this tool will be useful to characterize the paste of ceramics, enabling studies of sourcing and interaction. Central Plains tradition ceramics from the Central Plains of North America serve as the case study materials for developing this protocol.

Introduction:

The Central Plains tradition (CPt) has been defined for the east-central area of the Great Plains region of Nebraska and Kansas as well as portions of Iowa and Missouri for the time period of approximately 1000 AD to 1400 AD. CPt populations relied on distinctive tools, house types and ceramics attributed to numerous phases in the region including the Smokey Hills, Upper Republican, Nebraska and Itskari phases. For this study, I will be focusing on CPt ceramics specifically, the ceramic clay composition. This paper reports on the methodology that was developed to utilize a new X-Ray Diffraction (XRD) technology that allows for accurate data collection, with low levels of artifact destruction. This paper provides a brief overview of previous XRD work, describes XRD as it is now available, and gives a detailed account of the methodology developed, as deployed to characterize the ceramics recovered at two CPt sites, McIntosh (25BW15)

and Patterson (25SY31) in addition to the various demonstration studies conducted to provide insight into why the methodology was designed in this fashion.

The McIntosh site (25BW15) was discovered and excavated in 1987 to 1989 by the Nebraska State Historical Society and volunteers. It is the first Nebraska Sandhills site excavated along a lake in the region and is the only example of semi-permanent habitation site known for this time period and this eco-region. Characterized by grass-stabilized sand dunes with a mix of prairie grasses, the Nebraska Sandhills is a region that offers little in terms of ceramic or lithic raw resources. The McIntosh site is situated near the banks of Enders Lake. It includes a number of storage pits, a midden and evidence of a single structure via post molds (Bozell 1994, Koch 1995). The lithic assemblages show characteristics of the Itskari phase (AD 1100-1350) (Ludwickson 1978) with the sources themselves potentially coming from regions further to the west, including eastern Wyoming, northern Colorado and southern South Dakota (Koch 1999: 13). The ceramic assemblages resemble ceramics from the Upper Republican and Smokey Hills phases (AD 1000-1400), these phases being further south than the Itskari phase (Koch 1995).

The Patterson site (25SY31) was discovered in 1972 by Gayle Carlson and had excavations and analysis conducted by the Nebraska State Historical Society in 1977, 1984 and 1993. Located in Sarpy County, Patterson is consistent with Nebraska phase (AD 1050-1425) assemblages with the house construction design and structure type. Overlooking the Armburst Creek on a high ridge, the Patterson site is a collection of four structures, each showing different occupational periods (Bozell 1994, Bozell et al. 1999). Only three of these structures have been excavated, with evidence here suggesting that

there was some specialization on lithic production, these products most likely used for the purposes of trade in a network (Bozell 1994: 125).

The interest and focus on these two sites stems from the debate on interactions amongst CPt peoples. Initially, it was believed that movement and interaction amongst the CPt populations of these phases was fairly low, suggesting instead a larger community and more emphasis on agriculture (Roper et al. 2007: 325). Roper suggests a different hypothesis; that there was a lot more mobility and interactions between CPt populations, and these groups were smaller scale living as autonomous farmsteads that follow major stream and river systems from the Southeast to the Northwest. Through their first Neutron Activation Analysis (NAA) study on sites from the Upper Republican and Smokey Hills phases, Roper et al. (2007) examined ceramics amongst CPt sites, finding evidence for more interaction amongst these populations (Roper et al. 2007). Our study closely follows the basic framework of the study by Roper and colleagues, with more emphasis on site selection and developing a workflow for XRD techniques.

X-Ray Diffraction:

X-ray diffraction is a powerful characterization technique used in the analysis of crystalline solids that exhibit long range order, i.e. when the atomic positions are repeated in a regular fashion. When impacted by light or radiation, a 3-dimensional array of atoms, molecules or ions, cause the light to be diffracted, as described by W. H. Bragg and W. L. Bragg in 1913. This behavior is summarized by the expression, $n\lambda = 2d \sin\theta$ (Bragg's Law) where λ = wavelength of radiation used (in our case, Cu [Copper] radiation, $\lambda = 1.5408\text{\AA}$), d = interplanar spacing within the crystalline solid and θ represents the incident angle between the x-rays and sets of parallel "planes" in the crystalline solid. In

order for diffraction to be observed (constructive interference), Bragg's law must be satisfied (Figure 1).

Bragg's Law:

$$n \lambda = 2 d \sin (\theta)$$

where

λ is the wavelength of the rays

θ is the angle between the incident rays and the surface of the crystal

d is the spacing between layers of atoms

and constructive interference occurs when n is an integer (whole number)

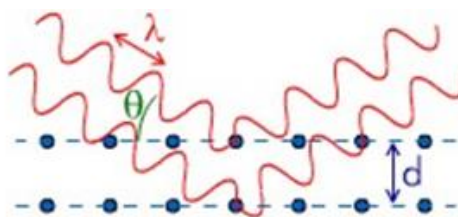


Figure 2.1: Bragg's Law (Figure 1: http://www-outreach.phy.cam.ac.uk/camphy/xraydiffraction/xraydiffraction7_1.htm)

When the x-rays are scattered by the electron clouds of atoms and constructive interference occurs, the result is recorded as a distinctive powder pattern, plotted as Intensity vs. 2θ , where 2θ is the sum of the angle of incidence (θ) and the angle of reflection (θ) (See Figure x). Powder patterns for pure phase or mixed powders exhibit peaks at specific values of 2θ (and consequently values of d) yielding a characteristic “fingerprint” that can be used to identify a crystalline phase or mixture of phases. The values observed for the d spacings are determined by the size and lattice centering of the crystal lattice. The intensities observed are determined by several contributing factors including the identity and positions of the atoms in the lattice, their interaction and absorption of the x-rays. The thermal motion of the scatterers as well as the geometry of the diffraction experiment can cause peak positions to shift slightly along 2θ .

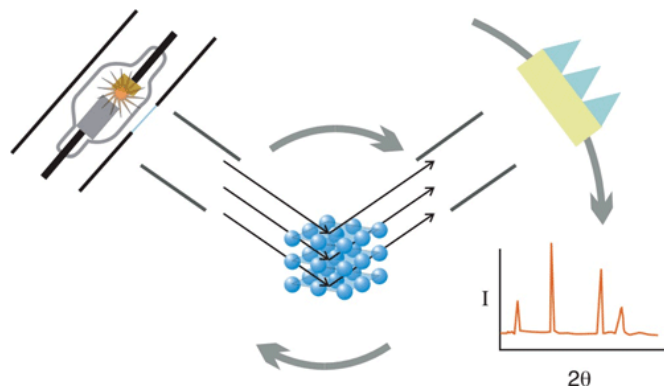


Figure 2.2: X-Ray Diffraction process (Figure 2;
<http://ees2.geo.rpi.edu/probe/Images/concepts/concept2.html>)

Figure x depicts a basic interpretation of how X-Ray Diffraction works. An x-ray source is provided and directed at the crystalline solid sample. Note that the sample does not need to be a single crystal, but can be a collection of crystalline solids present in a powder. The x-ray source directed at the sample diffracts based on the d-spacing and crystal lattices. These diffracted rays are measured at certain angles to view intensity. This in conjunction with the angle of incidence yields the 2θ plot, better known as the characteristic powder pattern of the sample. Figure y provides an example of what the detector actually sees, with the brighter rings indicating peak locations and the brightness of the rings indicating peak intensity. Newer XRD instrumentation removes this and directly translates the data into a powder pattern.

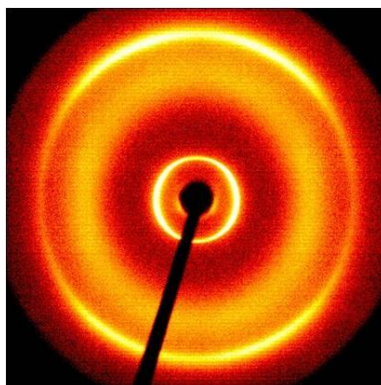


Figure 2.3: Detector View. Rings are translated into peaks along 2θ with the center of the scan being the lowest degree analyzed, and increasing 2θ as distance from the center is increased. (Figure 3; <http://nsm-lc-database.tudelft.nl/index.php?page=5>)

The measured powder pattern and its d spacings can be searched against a database of known crystalline materials in order to identify the phase(s) present in a samples. For example, for compounds with the elements of Zn and S (Zinc and Silicon), XRD can distinguish between two crystalline phases which give characteristic “fingerprints” as shown in Figure 2 and have dramatically different 3-dimensional structures. These structures differ in how the Zn and S molecules form 3-dimensional structures, the black being Wurtzite, a hexagonal ZnS structure, and the red being Sphalerite, a cubic ZnS structure (Figure 2). Figure 2 provides an example of the powder patterns for the different structures, and powder patterns are read by looking at the locations of the peaks along the 2θ .

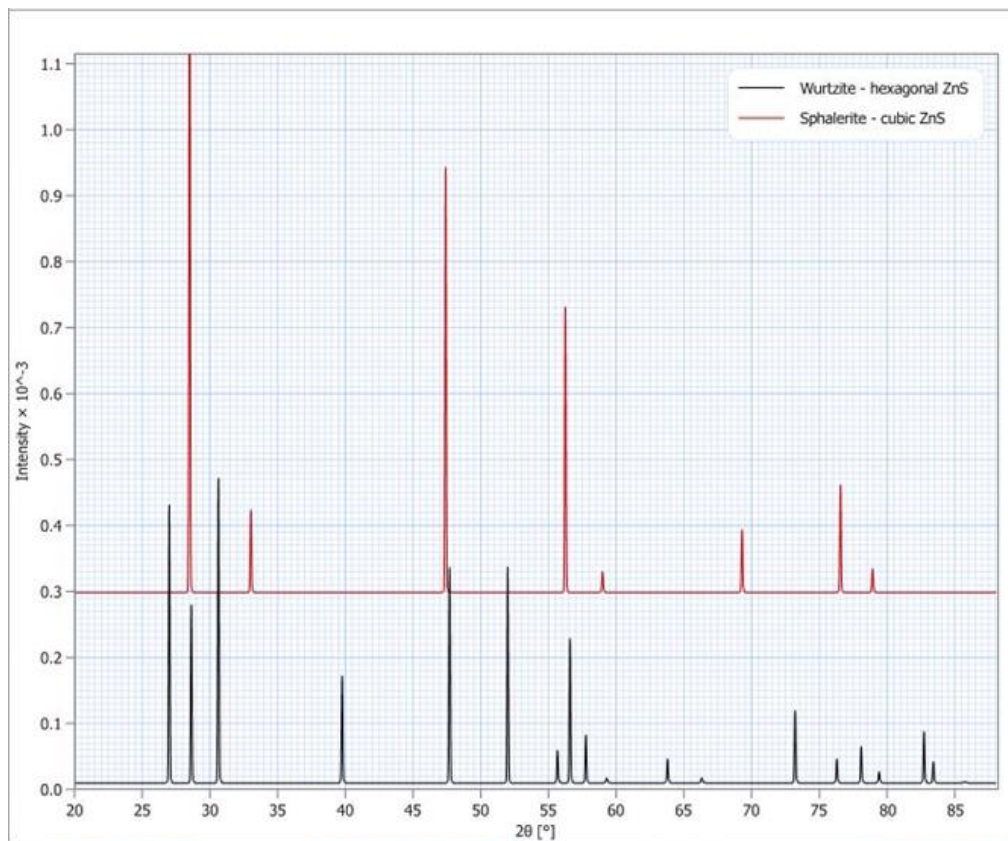


Figure 2.4: XRD Comparison of two different ZnS structures (Markvardsen 2010)

Essentially, XRD looks at how elements and atoms are making 3-dimensional structures, and these 3-dimensional structures are formed by minerals, crystals, compounds and chemicals. XRD also views everything in a sample, so in terms of clays, it is looking at all the minerals, compounds and amorphous material that composes the clay. Here, I am looking at peak locations along the powder pattern, which is a characteristic set of peak locations along 2θ that when combined, characterize the material. As clays are made up of more than just one material, these clay powder patterns are showing all these materials and help to create a characteristic “fingerprint”, or powder pattern, that is specific to that clay source.

Additionally, this methodology includes use of a heat stage module (Figure 3 & 4), a small beryllium dome with a platinum-rhodium strip used to heat powder samples to temperatures in excess of 1000°C. This heat stage module allows us to take small scrapings of samples (approximately 0.1 grams) from the unmodified artifact and refire it to a particular temperature. Refiring is required for XRD when analyzing ceramic artifacts for two primary reasons: the first is to remove any organic material such as grass that may have been used as a temper material; the second reason is to standardize the maximum temperature that all the samples reached. Because XRD is looking at the 3-dimensional structures that the molecules of the minerals and materials are forming, the temperature a sample was fired at is incredibly important, as minerals and materials undergo phase transitions (i.e. changes in the 3-dimensional structure), and often these changes are permanent; once a temperature range for a phase transition is achieved and the phase transition occurs, even after the sample is allowed to cool back down to room temperature it will not change back. By standardizing the maximum temperature all the

powder samples achieved to something at a much higher temperature than what would have been used in the ceramics initial production, it means that if the samples are of the same clay source, they will have undergone the same changes and thus have the same powder pattern. Without refiring, two ceramic sherds that used the same clay source, but had two different firing temperatures may have two different powder patterns, simply because one sherd underwent a phase transition at the higher temperature, while the other sherd did not undergo the phase transition.

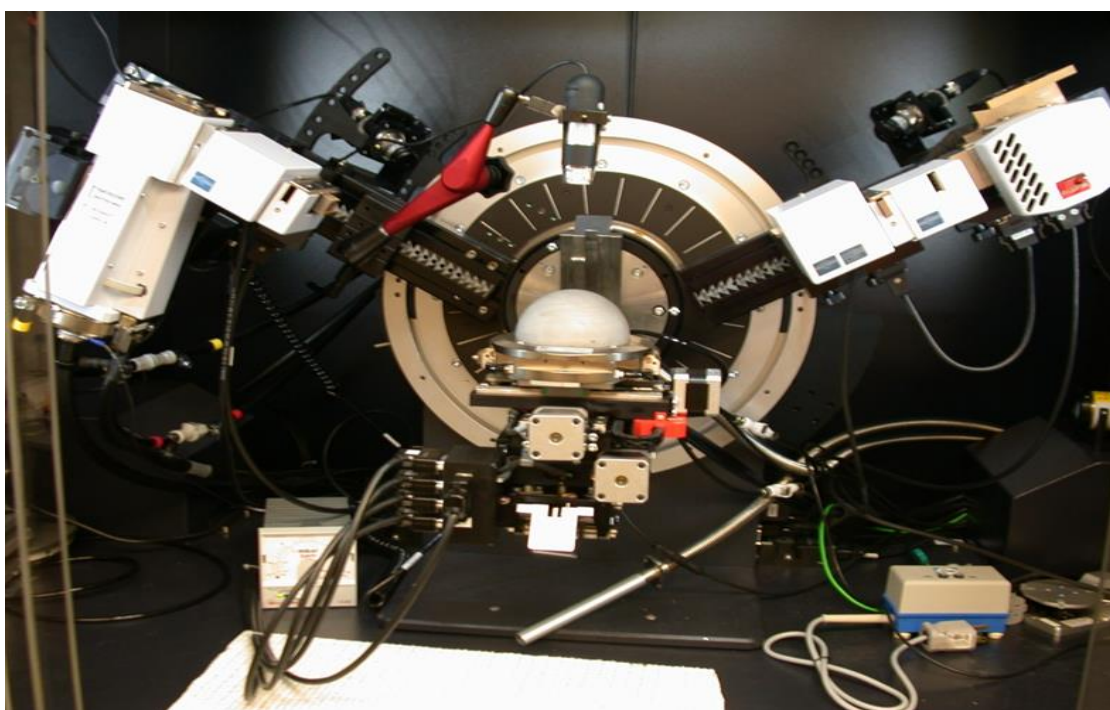


Figure 2.5: Bruker D-8 Discover DaVinci with Heatstage module and dome mounted (Wake Forest).

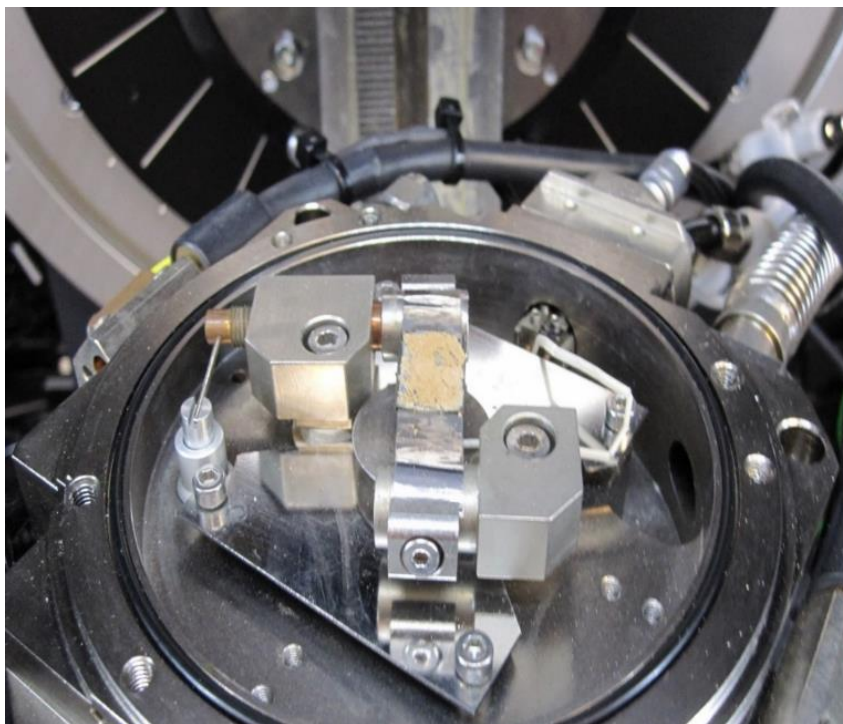


Figure 2.6: Bruker D-8 Discover DaVinci Heatstage Module Platinum-Rhodium Heater Strip with mounted powder sample (Wake Forest).

X-Ray Diffraction and Archaeology:

X-Ray Diffraction is not a new technology to archaeological investigations. In the past, and even more commonly today, XRD is a commonly used technique for archaeological research in a variety of research subjects. XRD has been used to examine and characterize lithics (Graetsch and Grunberg 2012, Schmidt et al. 2012), pigments (Burgio et al. 2002, Martinetto et al. 2002), cosmetics (Martinetto et al. 2002), the structural integrity of ancient hair (Tsoucaris and Bertrand 2002), and metal ores (Knorr and Yang 2011). The methodology has proven useful for archaeologists looking at a variety of materials that require a specific focus on the structural characterization of the composition of those materials. Additionally, XRD has been a useful tool for archaeological studies focusing more on ceramics.

In relation to this article, research has been conducted into XRD and clay firing temperatures. Rasmussen et al. (2012) have used XRD to determine original firing temperatures by examining ceramics and burnt clay from a variety of sources in Northwestern Argentine region, looking at the Late (AD 900-1450) and Inca (AD 1480-1532) periods (Rasmussen et al. 2012: 1705). By testing both the sample via XRD in conjunction with magnetic susceptibility studies to determine original firing temperatures, Rasmussen's study monitored sudden shifts in the susceptibility and compared those changes with powder pattern changes monitored with XRD. The application of the methodology showed that a combination of the techniques can be used to accurately determine original firing temperature to within 25.8°C.

Additional studies of ceramics and XRD often include examining the specific mineralogy present in the clays of the artifacts, such as with Herbert and McReynolds (2008) research into Woodland pottery located in the Carolina Sandhills. XRD was employed in a semi-quantitative analysis of certain mineralogy present in clays, with emphasis on K-feldspar, quartz lepidocrocite, gibbsite, plagioclase and amphibole. These results, in conjunction with previous Neutron Activation Analysis (NAA) work, helped explain geochemical patterns detected in the NAA data alone (Herbert and McReynolds 2008: 117-118). In this study, Herbert and McReynolds were focused on specific minerals present in the clays to help with their sourcing study, and followed specific protocols in sample collection to acquire what was needed.

XRD Protocol Concerns:

In order to develop a methodology using the heatstage module, we wanted to analyze the other workflows that have either been used for ceramic analysis, but are

highly destructive, as well as the setup of the XRD unit itself. It is also important to determine which setup and configuration of the XRD machine itself would be optimal for this methodology, beyond just using the heatstage, as the different configurations and setups for this particular model of X-Ray Diffraction unit affects sample surface scanned, penetration beneath the surface of the scanned sample, length of time to get high quality data, etc., and thus these demonstrations were used for that purpose as well.

As mentioned the D-8 Discover DaVinci unit by Bruker is modular, with the ability to swap and change a large number of variables. To examine the optimal setup, a collection of artifacts that were unproven artifacts provided by the University of Nebraska's Anthropology Department were analyzed using two basic setups of this unit, the Bragg-Brentano setup and the Goebel Mirror Setup. The Bragg-Brentano setup for the X-Ray source and detector features a deeper penetration into the artifact, hitting sample that is beneath the surface layer, however the surface area that is hit by the beam is much narrower. The Goebel Mirror set up projects the beam in such a way that the surface area is much larger, however it does not have nearly the same amount of penetration beneath the surface layer that the Bragg-Brentano setup has. Even though a larger surface area of the sample is hit via the Goebel Mirror method, to get similar peak pattern resolution, the scanning process needed to be longer than the Bragg-Brentano setup.

As mentioned above, refiring the clay is a requirement to get accurate and consistent results when using XRD on ceramics. A ceramic analysis XRD method that has shown success in past studies (Thacker 2014), but is also highly destructive to the artifact and ceramic clay, involves taking a sizeable piece of the ceramic to be analyzed

and refiring it in a kiln to a particular temperature. Typically, the selected refiring temperature is at the highest, or slightly above the highest that would have been achievable based on the original ceramic production procedures and available resources to the ceramic makers. Afterward refiring the artifacts, the sample to be scanned is removed from the refired artifact. With more recent XRD equipment, the sample required can be as small as a few milligrams, collected by scrapping off some powder via a microscope.

This methodology has shown the ability to accurately categorize raw clay samples by the bedrock of the area, as well as group clays of ceramics categorically (Thacker 2014). However, this technique is very destructive to artifacts, requiring a large amount of the artifact to be refired in a kiln. Thus, with access to new X-Ray Diffraction technology, particularly the heatstage module available on Bruker's D-8 Discover DaVinci, we have developed a new methodology that minimizes the destruction of artifacts, but allow us to collect data that has no decrease in the accuracy or replication potential of the data acquired.

Sample Preparation:

Sample preparation for the heatstage module was developed to maximize collection of the clay paste while minimizing the damage to the artifact itself. Razorblades and sandpaper were used to along the broken cross section to collect the clay material of the artifact. This allowed for the clay paste of the artifact to be collected, while minimizing damage to the face surfaces of the sample. The following procedures were used for powder sample collection:

Two new razorblades and, in some rare cases, a clean fin- grained piece of sandpaper were used to collect material from each artifact. The first razorblade and clean piece of sandpaper was used to remove the outermost layer of the artifact, collecting none of the powder to be used for analysis. This is done to remove any potential contaminate, microscopic residue or other substance that may not be part of the clay or ceramic. The second clean razorblade was used to collect the actual powder sample to be used in the scanning process. We opted for slightly higher amounts of powder (0.1 grams) than what is required for the bare minimum to collect reliable data (approximately 0.03 grams) in order to quicken scan time and increase resolution (Figure 6). The powder is collected from the broken cross section, aiming for the paste in the center of artifact.

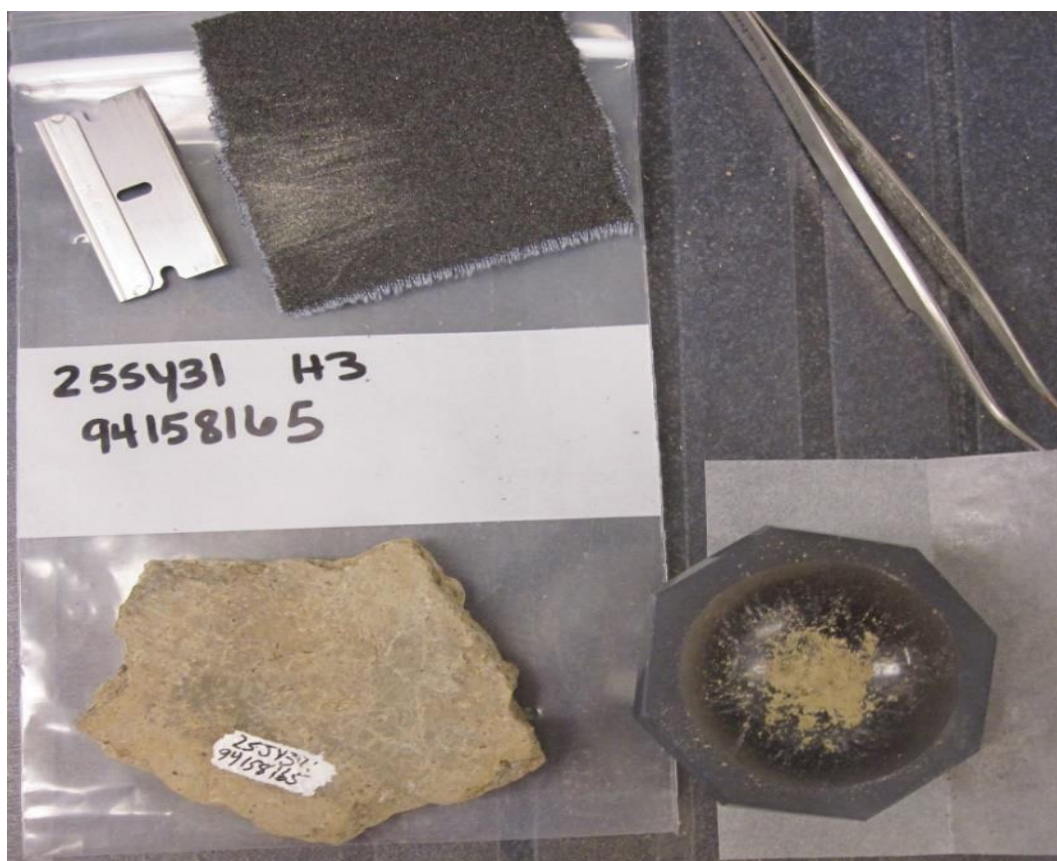


Figure 2.7: Sample collection process and Sample size comparison (bottom right)

The powder sample is first collected onto glassine paper, a clean piece given to each artifact, while the sample is scraped. This collected powder is transferred to a mortar and pestle where tweezers are used to remove any large inclusions that may have been included in the artifact as temper material (gravel, stone, etc.). The sample is then ground it into a finer powder. For the heatstage, a finer powder is preferred so the powder is more evenly spread on the strip and a flatter surface is used for the scans. A rougher surface can cause the peaks on the powder pattern to occasional shift, decreasing the accuracy of the data.

To mount the sample onto the heatstage, I add ethanol to the powder in the mortar and pestle to turn the powder into a slurry, then using a glass pipette we spread the sample evenly over the platinum-rhodium strip that acts as the heating surface of the heatstage module. The strip that can be covered is approximately 20 millimeters in length and 5 millimeters wide. A very thin layer of the slurry is placed over this entire surface, and the ethanol is allowed to evaporate, leaving just the powdered sample. We then take a photo of the sample before any heating and further modification of the sample is done.

Heatstage Protocol Verification:

The heatstage module used on Bruker's D-8 Discover DaVinci Diffraction unit (Figure 3 & 4) functions by a platinum-rhodium heater strip connected to a thermocouple. The heaterstrip can be heated to temperatures in excess of 1000°C and also allows small amounts of powdered sample (according to specifications, sample as small as 0.03 grams of powder) to be heated to these temperatures. The sample and heaterstrip are enclosed in a beryllium dome, which allows the x-ray source to pass through it so that the sample can also be scanned while being heated in real time, not only before heating and after. The

methodology developed for this study wants to examine the potential this module has for minimally destructive analysis on ceramic artifacts. In order to get the best possible results, three tests were conducted to find the optimal setting to be used for the heatstage.

1. Effects of Temperature Change Rate on Results

Before we started scanning ceramic artifacts, we wanted to be certain that results collected on with the heatstage module would be accurate. I conducted a series of experiments designed to test the how the heatstage would work with ceramic powder. The first experiment focused on heating rate, that the sample would not move and that the sample would indeed undergo the required phase changes. This study was conducted by placing sample collected from unprovenienced and unknown ceramic samples provided by the University of Nebraska–Lincoln for initial testing purposes onto the heatstage and increasing the temperature up to 700°C at different rates, starting at 10°C a minute as the slowest, and the fastest being 50°C a minute. With faster ramping, the sample may move or shift unexpectedly because of the heater strip changing shape. Slower ramping also allowed heat transfer from the heater strip to the sample to occur, without the sample buckling

2. Refiring Temperature Required

The second experiment analyzed the particular temperature we wanted to refire the samples too. Following Roper et al. (2007) in which they specifically mention a temperature of 750 ° C, most likely done to remove organic matter, we used ten ceramic powder samples collected from McIntosh and Patterson artifacts. We collected the samples and scanned each sample at room temperature before any refiring. We slowly fired each ceramic up to 750°C at a rate of 10°C per minute and let the sample sit at

temperature for approximately an hour before taking a forty-minute scan of the sample at temperature; each powder sample therefore spent a total of approximately one hour and forty minutes at 750 before cooling down to room temperature, allowed thirty minutes to sit at room temperature and scanned again. All three collected powder patterns were compared to each other to monitor if the phase transitions we want to expect to occur actually happen. As mentioned previous in this paper, theses phase transitions are required to make sure that we have accurately standardized all the samples to a higher temperature than what would have been achieved during their production. Sample 25SY31 H3 94158165 (Patterson) was the only sample that showed no expected phase transition of the scanned ten samples. The experiment was repeated to incrementally increase the temperature at by 50°C per stage starting at 800°C. This experiment was continued until the phase transition occurred. For 25SY31 H3 94158165, the phase transition occurs between 850°C and 900°C, thus 900°C was selected as our maximum refiring temperature. This was done to make sure that all samples underwent a phase transition so that we could be sure we had attained a temperature higher than that at which the ceramic vessel was originally fired.

3. Refirng Duration Requirements

The next experiment considered how long the sample would need to be held at a specific temperature. Following Rasmussen et al. (2012) on firing temperatures and burnt clays, we analyzed how long samples would need to sit at particular temperatures to undergo all the necessary phase transitions (Rasmussen et al. 2012). For example, some phase transition happens rapidly over the course of minutes, others unfold over hours. After the first scan was taken, the machine automatically began heating the sample to

900°C at a rate of 15 °C per minute. When the final refining temperature of 900 °C was decided upon following heating experimentation to monitor at what temperatures certain samples would undergo phase transitions, we determined that approximately thirty minutes at temperature would give us the desired effect after monitoring the sample in real-time using a series of scans, and noting that no additional phase transitions occurred after this.

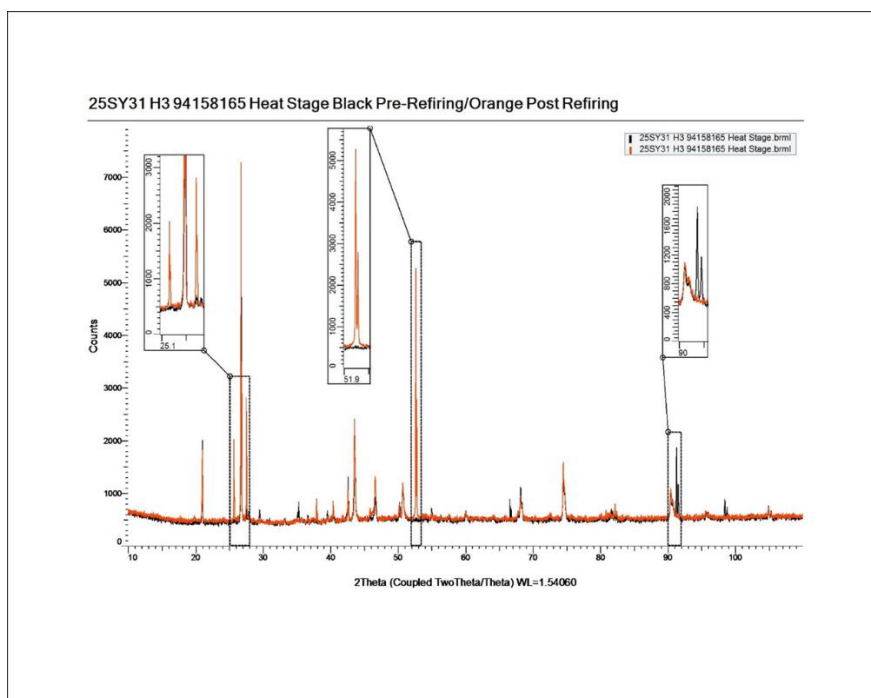


Figure 2.8: Patterson site (25SY31) H3 94158165 artifact powder sample undergoing expected phase transitions from pre-refiring (black) to post-refiring (orange)

Heatstage XRD Data Collection:

The scanning process is as follows. The heatstage is first taken to 30°C (approximately 86 °F) to make sure the heatstage is working properly, and the sample is scanned at that temperature before any other heating or modification is done to the sample. This scan is used after the experiment to compare with the second scan to make sure that the clay in the ceramic had undergone a phase transition. The scans take approximately 40 minutes from start to finish, scanning range of 20 degrees to 100

degrees along the 2θ range. The samples are allowed to heat up to 900 °C and allowed to sit for thirty minutes before a scan is taken. In addition to standardizing the firing temperature of all the samples under the same conditions, refiring is done to remove organic material. Organic material can be added to a ceramic as a temper material, often in the grasses. The refiring process will burn out this organic material, which in addition to removing large inclusion during sample preparation, minimizes the impact of temper material that might be present in the sample. After the sample has finished the refiring process has finished, the sample is allowed to cool to room temperature (a controlled temperature of 30 °C) and allowed to sit for thirty minutes before the final scan is started.

This second scan follows the exact same configuration as the first scan, except that the sample has undergone heating and the desired phase transitions due to the refiring process. This second scan is then compared to the initial scan taken before to make sure that a phase transition has occurred.

The heatstage is then turned off, the beryllium dome removed and a photo is taken of the refired powder. The sample is removed from the platinum-rhodium strip, wrapped into the small piece of glassine paper and placed into a smaller bag inside the bag containing the artifact, in order to preserve the refired powder sample if it is needed in the future for research or comparative results.

The scan data is then brought over to Bruker's Diffraction software package to process the data and display the powder patterns. Powder patterns from other artifacts can be brought in and compared, as can the powder patterns in a database that contains information on a collection of materials, chemicals and compositions. For this case study, Eva is used to compare one artifact's powder pattern to another artifact's. Based on peak

additions or deletions as well as peak shifts (slight movement along 2θ) of the powder patterns, we are, by eye, able to group the ceramics. While peak intensity can be used to define different elements present in the sample, for this case study, we focus only on the 2θ values to get an initial sense for whether this methodology and analysis technique will be useful for Central Plains tradition pottery (Figure 7).

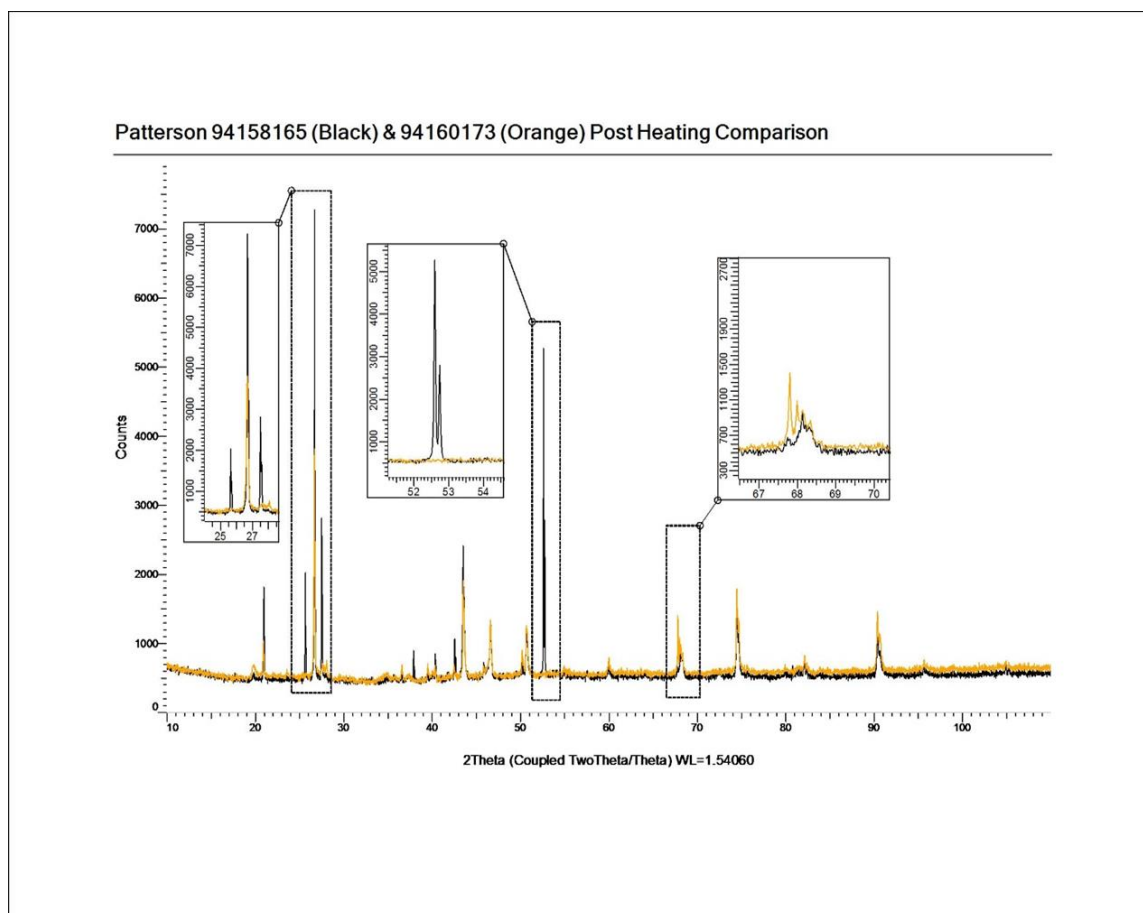


Figure 2.9: Example of Peak Pattern Comparison between Central Plains tradition Patterson site samples 94158165 (Black) and 94160173 (Orange)

This methodology was repeated twice using separate powdered sample collected from a separate location on the artifact on a number of the artifacts. The post-refiring powder patterns were then compared to one another to test for consistency. If the two scans from the two separate powders matched one another, we could accurately say with

a high level of confidence that we would consistently get consistent results on the following samples.

Conclusions:

With the development of new technology and advancements in the speed of data acquisition while maintaining a high level of accuracy, X-Ray Diffraction as a technique by itself can allow for accurate sourcing of clay resources and their characteristic powder pattern. Through the methodology that we have developed for our case study focusing on the use of the heatstage module, XRD studies done in archaeology no longer need to be nearly as destructive, cutting out the need for refiring large sections of ceramic artifacts in a kiln and instead refiring a small amounts of powder scrapped from the artifacts and scanned in real-time via the heatstage. This methodology has allowed us to start examining ceramics from the Central Plains tradition while keeping the process replicable and minimally destructive, and will be used to begin examining the interaction amongst CPt tradition sites and populations by testing to see if there are structural differences in the materials making up the clays used for ceramic production amongst CPt populations. Following this, monitoring of the movement of these clay sources may allow us to better understand the flow and interaction of CPt populations.

Future for Study:

There are a multitude of potential uses that we can use the scan results for. For the preliminary results in our study, we will be using the most basic function of the data, a comparative grouping of the samples based on the artifact's individual powder pattern. We will be applying this methodology to a collection of samples from Central Plains tradition sites, with a particular focus on the McIntosh site (25BW15) located in the

Nebraska Sandhills and unassociated with any particular CPt phase commonly defined as the lithic assemblages show Itskari phase characteristics, and the ceramic assemblages show evidence of Upper Republican and Smokey Hills phases characteristics. For this case study, we will also sample a smaller collection of ceramic artifacts from the Patterson site (25SY31) located in the eastern part of Nebraska, with structure construction and design placing it into the Nebraska phase of CPt peoples, and additionally showing signs of trade with Upper Republican phase CPt populations.

We plan to apply this methodology to a larger sampling of ceramic artifacts from CPt sites, and eventually try to map out clay movement in ceramics, particularly the movement of clay into the Nebraska Sandhills region focusing on McIntosh. Following this XRD methodology, we believe it is possible to map out where the ceramic clay used on the production came from, if not to a very specific source, at the very level of region to region. This would allow for a better basic understanding and mapping of interactions between CPt people, similar to Roper et al. and their NAA study (2007).

Acknowledgements:

We would like to acknowledge Dr. Cynthia S. Day of Wake Forest University's Chemistry department, whose assistance and knowledge helped in the development the methodology as well as the assistance provided in processing the data gained from the method. This work is an extension and continuation of work started at Wake Forest University's Department of Chemistry and Anthropology Department, which supplied assistance in experimentation, the protocols and equipment. Nebraska State Historical Society provided the artifacts and their expertise in sample selection. Thank you to these organizations. An additional thank you to the Champe/Weakly Funding Program of UNL as well as the Berueter Fellowship and Dana Deger Memorial Scholarship for funding this project.

Chapter 3:**Initial Results from Case Study of Central Plains Tradition Ceramics Analyzed Using X-Ray Diffraction in an Attempt to Monitor Interactions Amongst CPT Populations****Abstract:**

This paper presents the results from X-Ray Diffraction (XRD) analysis of Central Plains tradition (CPT) ceramics, testing the viability of XRD as a useful tool for characterizing clays and ultimately differentiating different clay sources used in the production of CPT ceramics. This paper presents the XRD data obtained for XX ceramic sherds. It discusses, the implications of the data for understanding of ceramics from the Central Plains tradition and the interactions amongst CPT populations.

Introduction:

This paper reports the results from a case study focused on examining the viability of X-Ray Diffraction (XRD) as a method to group Central Plains tradition (CPT) ceramics based on their unique atomic structures. As elaborated upon below, the Central Plains tradition is a culture history taxonomic unit used to describe groups of people who lived in the Central Plains region, in particular the area of Nebraska, and northern Kansas during approximately 950–1450 AD. Materially, these groups are defined by their wattle and daub, semi-subterranean square structure construction as well as their semi-sedentary lifestyle with differed from previous groups. This case study presents the initial results on groupings of a selection of ceramic sherds based on the atomic structures of the minerals

and materials present in the clay used in their production. The overall goal of the study this case study is to continue to examine the clay sources used in ceramics and monitor their movement by looking at each clays characteristic minerals and materials present in them, following Roper and colleagues (2007). Their research used Neutron Activation Analysis (NAA) to characterize ceramics from a number of CPt sites located in northern Kansas and southern Nebraska. That paper laid the foundation for NAA to monitor interactions amongst CPt peoples by recognizing how distinctive ceramic clays were distributed among and between CPt sites.

This study closely follows the NAA work done by Roper and colleagues (2007), whose focus was on CPt sites along the Kansas and Nebraska border, presenting results from the McIntosh site and Patterson site (25SY31), located in an area north of Roper's work. Where Roper and colleagues relied on NAA, I rely on current generation X-Ray Diffraction (XRD) for analyzing the atomic structures of minerals and materials in ceramic pastes. XRD examines the 3-dimensional structure of materials, minerals and chemical compounds, all of which are the components that make up clays.

Central Plains Tradition Phases and Interactions:

The Central Plains tradition (900-1450 AD) is a taxonomic unit defined by archaeologists to refer to populations that embraced a more sedentary lifestyle, relying on growing their own food and living in more permanent structures in the eastern two-thirds of Central Plains (Strong 1935). The origins of these people are still debated (Roper 1995, Wedel 1986), however they show shifts in lifestyle, habitation pattern with additional changes to tool kits to better adapt to plains lifestyle as compared to previous populations both in the Central Plains and in the surrounding area. Following McKern

(1934) and with much subsequent discussion (e.g., Blakeslee 1999; Lehmer 1954), variations in material culture and geographic provenance have been used to define various aspects or phases within the Central Plains tradition (Figure 1). These phases include the Itskari/Loup River (1250-1450 AD), Upper Republican (900-1400 AD), Smokey Hills (900-1400 AD) and Nebraska (1050-1425 AD) phases (Figure 2). While originally defined as aspects (as per McKern 1934), these taxa were later converted to phases (Brown 1966). Since then, others have attempted to limit these phases regionally, or to subdivide them further and recast them into other phases (Blakeslee 1999; Krause 1969), though these new definitions have never gained any real traction (Roper 2006).

These different taxa are defined as based on variation in the assemblages, including chipped and ground stone tools, ceramic assemblages and faunal remains (Strong 1935). The ceramics in particular are of interest in this study, and while difficult to detect, traits that discriminate between the phases include rim thickness and design, the presence/absence of handles and the overall density of the ceramic assemblage at a site (Roper 2006: 111-112, Sigstad 1969, Strong 1935). Additionally, there is a component of artistic choice by the potters, most likely women, that is distinctive between certain phases, as Sigstad (1969) demonstrates in comparing the Mowry Bluff site (Upper Republican phase) and the Nuzum site (Nebraska phase). Sigstad finds that the ceramics at Mowry Bluff have more elaborate decoration, with those decorations restricted to around the rim (Roper 2006:112). Beyond the rim design and decoration, other traits include a larger representation of ceramics present in assemblages at Upper Republican phase sites in addition to evidence suggesting a higher firing temperature as compared to Nebraska phase sites (Sigstad 1969: 98). These traits are considered to be diagnostic for

ceramic assemblage differences between the various phases that make up the Central Plains tradition (Strong 1935: 256-257). However, these traits are not mutually exclusive to each region; there are sites that contain pottery and ceramic assemblages that do not match the typical characteristics of the phases. To complicate matters further, distinctive phase traits may not always have discrete geographic distributions. The McIntosh (25BW15) site, for example, one of the two sites used in this study, lies to the northwest of other defined phase localities; its assemblage resembles assemblages from other phases.

It is important to understand the geographic area and defining characteristics of these phases for this study because of how these taxonomic phases relate to the two principle theories on the interaction amongst CPT populations. The initial principle theory was that these phases reflect communities with distinct boundaries and with very little in the way of mobility or trade between these areas (Strong 1935, Wedel 1986). It was believed that the populations would live in hamlet pattern settlements, with structures scattered individually or in small clusters of up to six structures within several hundred yards of each other and all structures would be close to a water source of some kind (Wedel 1986: 100). This was the model used by most studying the Central Plains tradition and its' associated sites until recently.

In addition to a settlement pattern with defined borders and less mobility or interaction amongst the larger CPT populace, agriculture is an integral part of the Central Plains tradition. Indeed, there is a host of evidence that supports this theory that agriculture and horticulture were indeed an important part of Central Plains tradition subsistence. For example, Ludwickson (1978) notes the proximity of CPT sites to streams

and tributaries supporting an agriculturally-based subsistence. Wedel (1986) indicated that the climate may have changed around this time, equating to more rain in the area, likely leading to more support for maize cultivation (Wedel 1986:98). Subsistence and food is also considered to be one of the major trading factors present amongst CPT populations, as noted by Blakeslee (1978), who argues that food items appeared to have been traded, even amongst populations that were already providing similar resources for themselves (Blakeslee 1978: 140).

Roper's (1995, 2006, 2007) work, however, challenges these theories, arguing for a smaller scale settlement pattern of individual, autonomous farmsteads with a much higher degree of mobility, and less emphasis on agriculture. Roper suggests that agriculture was an adaptive strategy used in conjunction with other subsistence strategies, and indicating that these taxonomic definitions are "just arbitrary divisions of a continuum" (Roper 2006: 106). In most of her work, Roper continues to use these taxonomic names, but purely as a spatial reference (Roper 2006). Roper et al.'s (2007) Neutron Activation Analysis (NAA) study on sites from the Upper Republican and Smokey Hills phases indicates that there was likely more interaction and movement between these two regions than what would be allowed for if the phases were, in-fact, distinct boundaries with very little in terms of interaction and mobility between them. By examining the ceramics and their elemental profiles via NAA and Principle Component Analysis (PCA) their results were not as definite as it was originally believed they would be; their results suggest that increased sampling and other analytical techniques used in conjunction with NAA would help remove some of the discrepancy (Roper et al. 2007:333).

Following the research conducted by Roper, the overall goal of this study is to similarly look at the clay used in the ceramics production, not as distinctive ‘characteristics’ used to define taxonomic phases, but rather, to monitor what and where, if any, differences are detected in the clays used in ceramic production, potentially pointing to unique origins. This paper presents the results of one possible method that can be used to look at the clays used in ceramic production, X-Ray Diffraction, which, like NAA, looks at the composition of the materials and minerals present in the clays. However, while Roper and colleagues study analyzed the elemental profile of the sample, XRD analyzes the atomic structure of the elements and compounds.

Materials

For this case study, two sites were chosen. One site, McIntosh (25BW15), providing a large sample of artifacts, allows for the examination of intra-site variation in ceramics. A second smaller selection of artifacts from the Patterson (25SY31) site, allows for a modest examination of inter-site analysis variation in ceramic pastes. The McIntosh site (25BW15) is located in the Nebraska Sandhills; the Patterson site (25HY31) is located in southeastern Nebraska outside Omaha (Figure 1). [Move detail about phases here.](#)

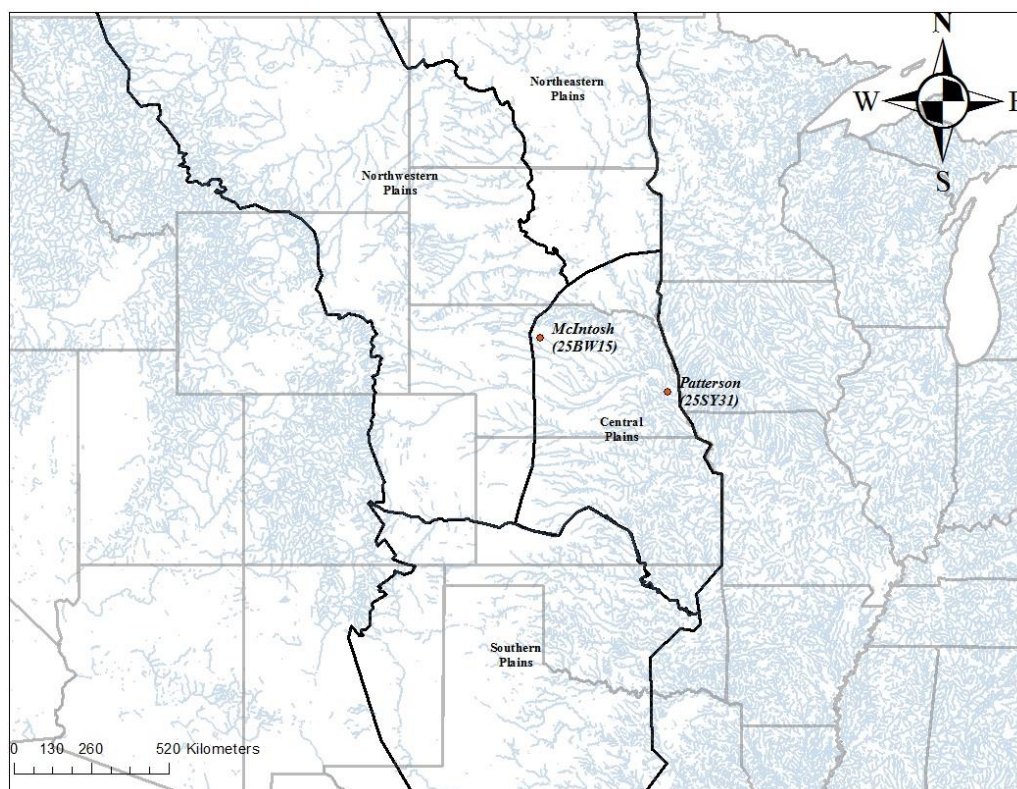


Figure 3.1: McIntosh and Patterson Sites in relation to Great Plains region and within the Central Plains subregion

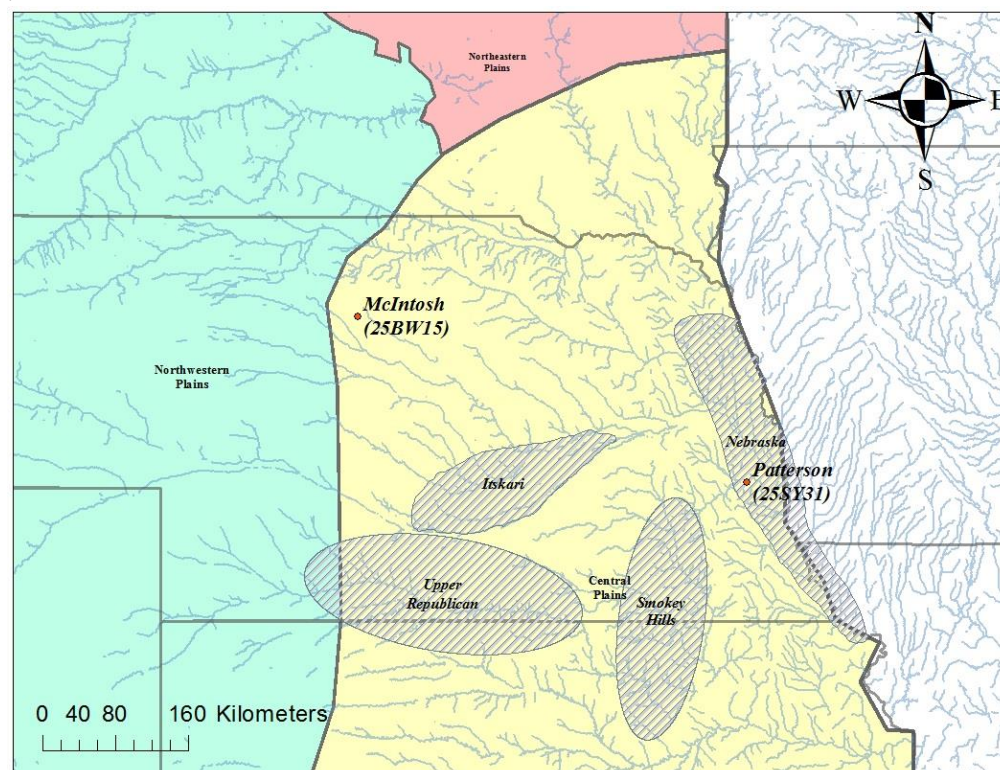


Figure 3.2: Map of McIntosh and Patterson Sites in Nebraska with Central Plains Tradition Phase Regions

McIntosh (25BW15)

Discovered and excavated in 1987 to 1989 by the Nebraska State Historical Society and volunteers, the McIntosh site is the first Nebraska Sandhills site excavated along a lake and is the only example of semi-permanent habitation in the Sandhills. Characterized by grass-stabilized sand dunes with a mix of prairie grasses, the Nebraska Sandhills is a region that offers little in terms of ceramic or lithic raw resources, save for along the river terraces, where water transported cobbles may be found and clay deposits may occur. Owing to the more plentiful nature of wetlands and lakes, there was most likely an increased amount of faunal sources around these areas as compared to the rest of the Sandhills region. The McIntosh site is situated on the banks of one of these lakes, Enders Lake. Features reported here include a number of storage pits, a midden and evidence of a single structure via post molds (Figure 2) (Bozell 1994, Koch 1995).

The archaeological remains include faunal remains, lithic tools and ceramic pieces. Based on macroscopic similarities, the lithic artifacts were sourced to locations to the west and north of the Sandhills, as seen for lithic materials from the CPT Itskari phase (AD 1100-1350) (Ludwickson 1978) assemblages, but also include materials from eastern Wyoming, southern South Dakota and northern Colorado (Koch 1999: 13). The ceramic assemblages, however, are, to the eye, similar to ceramics from sites defined as Upper Republican or Smokey Hills phase (AD 1000-1400) occupations, in southern Nebraska and northern Kansas (Koch 1995). In addition, an analysis of faunal remains by Koch (1995) while taking into consideration the amount of faunal remains found in comparison to other sites in the Sandhills and that the structure has basic elements of permanent CPT architecture (Bozell 1994), the McIntosh site is believed to have served

for one of two purposes. The first thought is that McIntosh served as a semi-permanent location used for mobile hunting of bison in particular (Bozell 1994). The second hypothesis is that McIntosh was an attempt to create more permanent settlements in the Sandhills region by CPt populations (Bozell 1994).

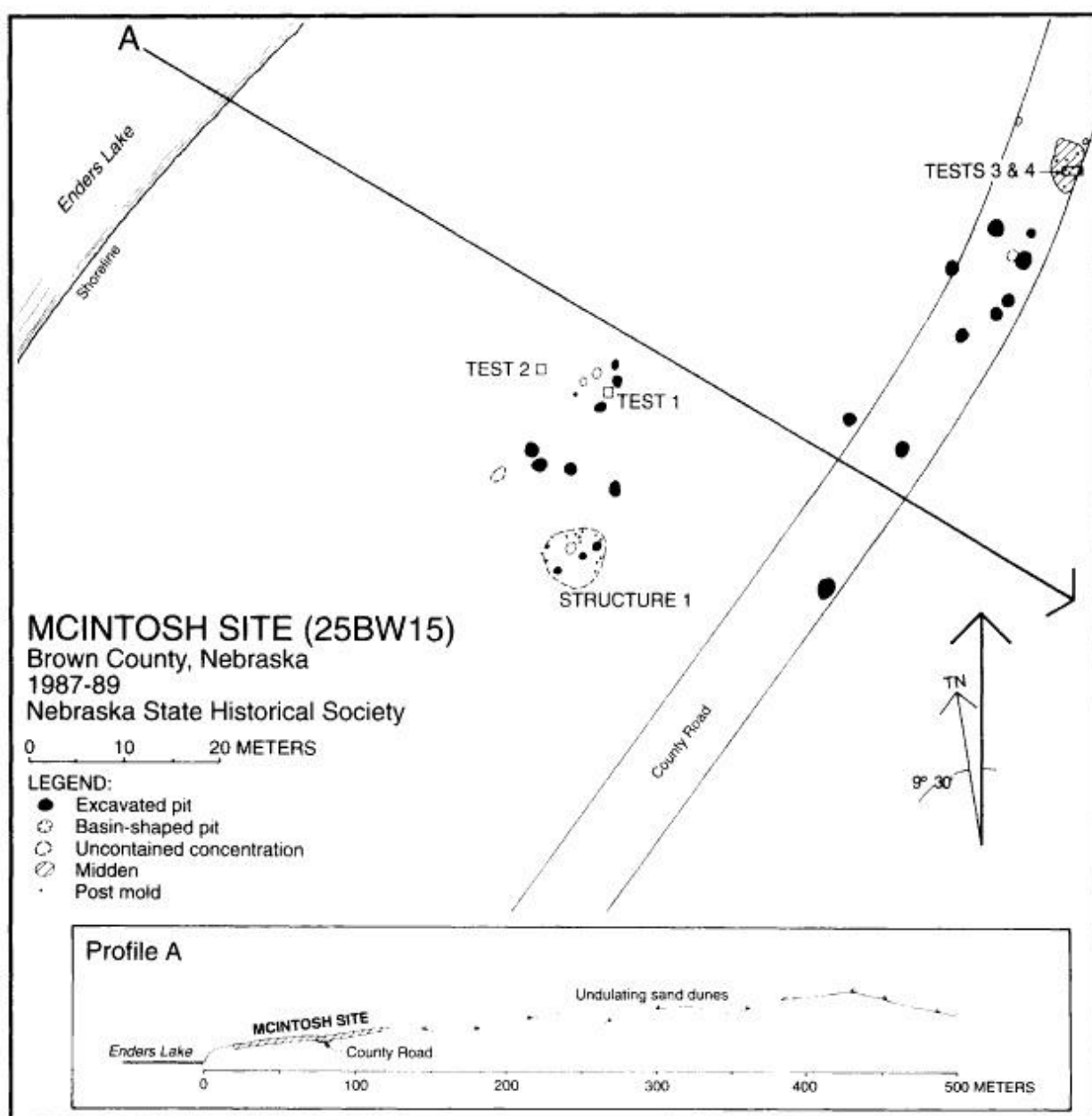


Figure 3.3: Map of the McIntosh site (25BW15) depicting locations of test excavations and features (Koch 1995; Figure 2, pp. 41)

Because of the great variation seen in lithic and ceramic assemblages, as well as the suspected paucity of raw resources available in the Sandhills region, the site was selected as the primary study site in this case study. As Koch noted (1995), the ceramic assemblages at McIntosh show traits from two phases, the Upper Republican and Smokey Hills, located in the southern Central Plains. It is possible that these particular ceramics came from those separate locations, via trade among or extended travel by Central Plains occupants. If this first option is the case, it is likely that different clay sources may have been used in ceramic production, which should be detectable via characterization studies, such as NAA or XRD. On the other hand, the clay sources throughout the Central Plains may be more or less the same, as they are derived from common sources with similar geology and lithology (bedrock) features. In this case, characterization studies will find no significant differences among ceramics, no matter their provenience. A final possibility is that the ceramics at each location were manufactured from local clay sources yet to be located while drawing from the Central Plains stylistic repertoire; characterization studies should reveal what exactly is different about materials and minerals present in the clays used for ceramic production.

Twenty sherds from different features were analyzed. The sampled features include Features F8801, F8802, F8806, F8701 and F8707, which are storage or refuse pits. The sherds are general ceramic body sherds that show a similar reddish-brown color. If further analysis is conducted, they will be grouped as potential outliers from the larger overall groups. This case study was also provided with four samples from the Wales Donation, a collection of artifacts known to be from the McIntosh site, however little other provenance information was given, and for the purposes of this study were given

individual numbers of 25BW15 Wales Donation 2481 1 of 4, 2 of 4, etc. These samples showed signs of pigmentation on the inner layer, thus a modified sample collection was used in order to obtain just the clay paste, with no potential contamination from the pigmentation. Refer to Appendix B with sample information.

Patterson (25SY31)

The Patterson site (25SY31) contributed four ceramic artifacts to this analysis. The Patterson site is located in southeastern Nebraska in Sarpy County and is defined as belonging to the Nebraska phase. Discovered in 1972 by Gayle Carlson and through excavations and analysis in 1977, 1984 and 1993 by the Nebraska State Historical Society, the site shows evidence of multiple occupations (Bozell 1994; Bozell et al. 1999; Brooks 2012). Four structures and a number of storage or refuse pits are reported, although only three of the structures have been excavated and of those three only one has been completely analyzed (Figure 3) (Bozell 1994).

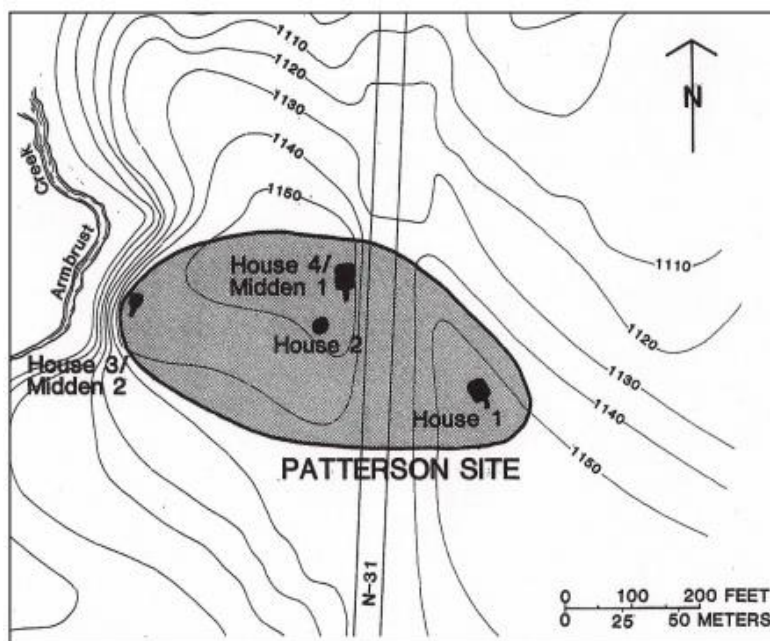


Figure 3.4: Four Structure locations at Patterson (25SY31) (Bozell and Ludwickson 1999: Figure 7, pp. 8)

Through the excavation of these structures, it was determined that the site was used more than once, and for extended periods of time. House 4 indicates that there may have been as many as 25 to 30 people residing there at one time, and there are even suggestions that the east and west halves had different construction styles, possibly meaning that an extended family was involved in the construction (Bozell 1994: 125). Archaeological remains found in these structures includes a wide variety of sandstone abraders, projectile point blanks and finished projectile points, and ceramic remains. The discovery of so many projectile points suggests that there was a specialized manufacture occurred here. Such specialization could have supported trade, as some ceramic vessels found here are from the Upper Republican phase as well as Mississippian; in addition, galena, a type of lead ore traditionally originating in Iowa and Illinois, was found here (Bozell 1994: 125). Excavation indicates that these structures were destroyed quickly by a fire, as layers of ash were found directly on top of artifacts remains. Indeed, it is suggested that some of the structures were occupied at the time of the fires as food remained stored on the floor and there were a number of stone tools that showed the signs of still being in production (Bozell 1994: 126).

The Patterson site ceramics were chosen as a smaller control sample to be included and compared to ceramics found at the McIntosh site due to the evidence that suggests there was already trade taking place at the Patterson site. Moreover, Roper and others highlight that interactions and trade amongst CPt populations most likely took place along stream and river networks, following a north and west route (Roper 1995; Roper et al. 2007). The four sherds from Patterson all vary in color, ranging from light

brown to almost black. All four sherds are body sherds, and were found in storage and refuse pits found in House 3. See Appendix A for more detail.

X-Ray Diffraction Method:

X-Ray diffraction is a powerful characterization technique used to analyze the crystalline solids in samples. A sample, composed of a 3-dimensional arrangement of atoms, is irradiated by an x-ray. The structure of the atoms and their electron clouds cause the x-rays to be either absorbed or diffracted, yielding a distinctive “powder pattern.” The powder pattern is a plot of Intensity and 2θ , with 2θ referring to the sum of the angle of incidence and the angle of reflection. These plots, or powder patterns, show peaks at specific locations along 2θ , these being characteristic “fingerprints” attributable to specific 3-dimensional structures. (In turn, the 3-dimensional structure of the solid may be owed to the current phase of an element or compound, with phase changing with temperature. For example, as temperature changes, H₂O changes phase and each would yield a distinctive powder pattern. Different combinations of peak locations can be used to specific mineral, chemical compound or material.

The methodology for this paper depends on the assumption that each distinctive powder pattern is associated with a different clay source or clay recipe. This study focuses on finding natural groupings of distinctive powder patterns as opposed to referencing powder patterns to a particular powder pattern. (To date, no such reference exists for ceramics, especially from the Central Plains.) The sherds are grouped based on the degree to which their powder pattern matches that of other sherds; these powder patterns will be saved for comparison with future Central Plains tradition ceramics that are analyzed in the same fashion. Because XRD as applied here looks at the ceramic clay

as a whole, the powder patterns are showing a complex combination of minerals, amorphous material and materials; everything that is present overlaid on top of each other and these combinations of overlaid peak patterns are what gives these “fingerprints” their characteristic powder pattern.

Our methodology incorporates new generation XRD technology and I used the Bruker’s D-8 Discover DaVinci unit at the Department of Chemistry at Wake Forest University. This new technology includes a heatstage module (Figure 5), a mounted stage in the machine that allows a sample of 0.1g of powdered sherds to be scanned while at different temperatures. (Figure 6). In contrast to earlier versions of XRD, which required larger samples and cumbersome multiple sampling-firing-scanning protocols, this technology relies on very small amounts of powder and the samples can have their temperature increased to a standardized temperature, allowing for all the samples to have the same opportunity to undergo the necessary changes in their 3-dimensional atomic structures. Thus, with this current generation of XRD technology, it is possible to obtain high quality data on the atomic structure of materials, while doing very little damage to the artifacts.

Sample collection involved the use of two razor blades per artifact; one to remove any exterior residue and the second blade for actual sample collection. Because the heatstage can work with very small samples, the amount of scraping done to the sherd is minimal. The powder is typically collected from the broken cross section of sherd, unless the sample is either slipped or has signs of pigmentation on one side. In these latter cases, the powder is collected either from the opposite face, or the clay paste is more carefully collected from the broken cross section. Any larger material that was included on the

ceramic, such as stone or gravel used for temper, is removed from the powder sample before grinding the sample in a mortar and pestle (cleaned after each use). The powder is mixed with ethanol, which evaporates quickly, to create a slurry that is then painted on the heaterstrip (Figure 5).

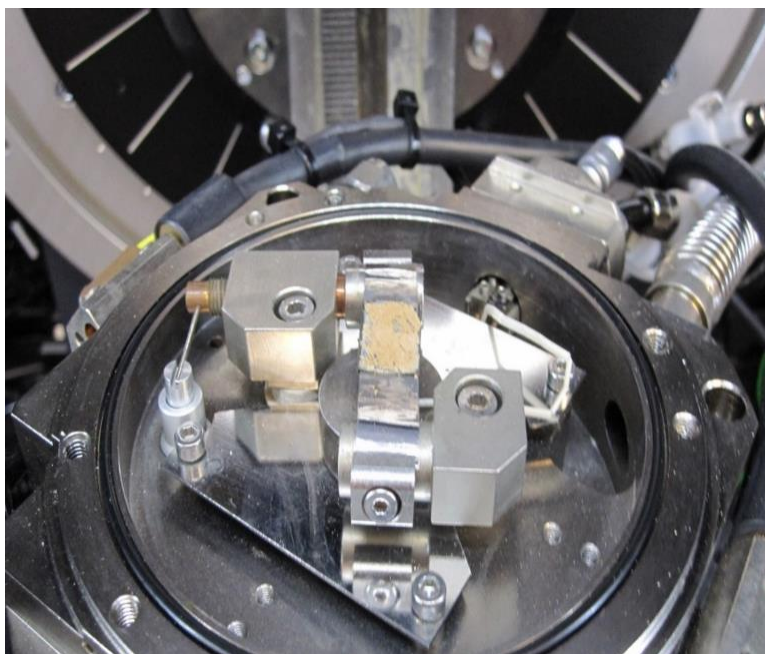


Figure 3.6: Bruker D-8 Discover DaVinci Heatstage Module with mounted sample.



Figure 3.7: Powdered Sample Size and Preparation

The X-Ray Diffraction unit with the heatstage module also used the standard Bragg-Brentano setup, scanning over a 2θ of 20° to 100° . The Bragg-Brentano setup allows for greater penetration below the surface of the sample, allowing for more of what is underneath to be examined versus other configurations such as the Goebel Mirror configuration. However, because the penetration is greater, the radiation beam? Occasionally went through the sample and hit the platinum-rhodium strip the sample was on, or, in some cases, hit the Inconel foil placed between the sample and the platinum-rhodium strip. Due to the potential of the scan picking up powder patterns from both the powdered sherd as well as the platinum-rhodium strip or the Inconel foil below the sample, separate powder pattern scans of just the strip and the foil by themselves were taken and their peaks taken into account during peak analysis of the ceramic powder patterns. After every scan, the Inconel foil and heater strips were cleaned thoroughly to eliminate possible cross contamination by the powdered sherds.

Increasing the temperature and ‘refiring’ the samples is a requirement for accurate XRD analysis due to the nature of what is being analyzed. The 3-dimensional structures of minerals and materials can change because of a variety of factors; one factor that has to be controlled for in XRD experimentation is the maximum firing temperature the clay in the ceramic has achieved. In XRD terminology, when the 3-dimensional structure of a material changes, it is known as a ‘phase transition’. The materials and minerals that make up clays have their own unique ranges at which these phase transitions occur and they are often permanent, i.e. the sample cooling down will not revert it to the earlier phase. In order to standardize the samples and make sure that all the samples have had the potential to undergo the same phase transitions, a refiring temperature higher than

what would have been attained is chosen. Without this important refiring step, it would be difficult to accurately determine different clay “fingerprints” on any two samples, as, hypothetically, two ceramic sherds may have been fired to different temperatures leading to each sample showing a different combination of phases of the materials present, even if the sherds had the same clay source used in the ceramic vessels’ construction.

The collected scan data was analyzed using the Diffrac.Eva software packages. The initial scan taken at room temperature was compared to the scan after refiring and cooling had taken place. These powder patterns were then individually analyzed, to monitor peak shift from non-modified powdered sample to the refired powder sample. This comparison between the pre and post refiring scans was done in order to monitor that a phase transition had occurred, and that any potential organic material had been burned out. Once completed, the post-refired powder pattern was then compared to other powder patterns from different sherds in the case study.

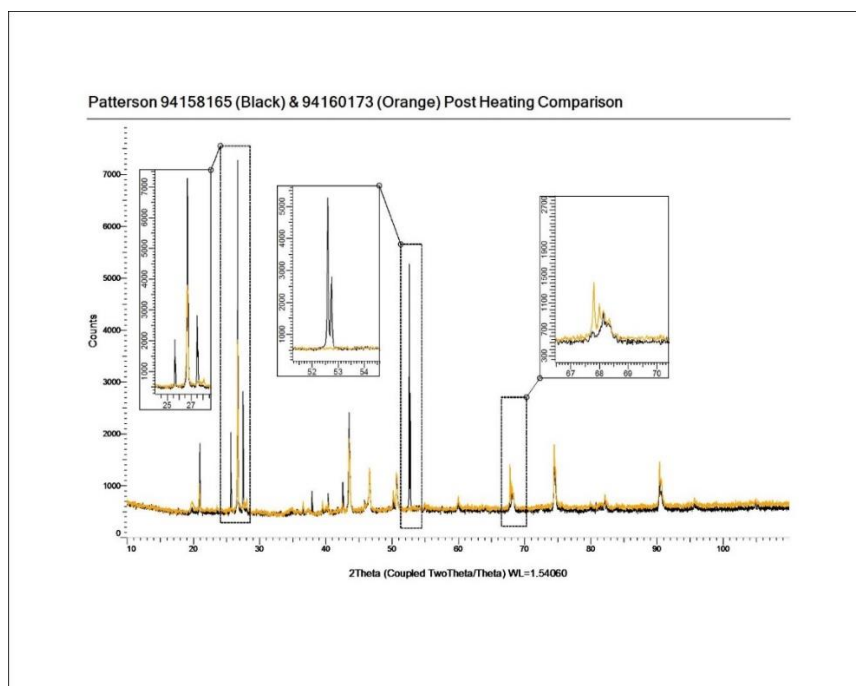


Figure 3.8: Example Powder Patterns from samples

Clays are a complex mixture of minerals and materials, making their powder patterns equally complex. Peak locations can vary slightly and still be considered the same material, particularly in the case of broader peaks that may be involved in the combination. Our analysis for the groupings of clay in the sherds focuses on these combinations of differences with a focus on peak additions and deletions present in the sample. By using Figure 7 as an example, the zoomed in sections show the kind of differences we are looking for, with peaks missing from 94160173 that are present in 94158165 and vice versa. It should be mentioned that these results have changed significantly once the refiring temperature was changed to 900 degrees Celsius, as 94160173 was not undergoing phase transitions due to a high enough refiring temperature not being used.

Initial Results:

Based on the powder patterns of these thirty sherds, four distinct powder patterns were identified (see Table 1). Two groups make up a vast majority of the samples scanned thus far. The third and the fourth group each contain a single sherd; the powder pattern of each include enough peak additions and deletions to indicate a unique structure. In addition, there are five outliers from Groups 1 and 2; these outliers have fewer or harder to detect differences in their powder patterns. Until further results are collected from more ceramic sherds and a more in-depth study of these particular sherds

Table 3.1. Preliminary X-Ray Diffraction Artifact Groupings (* denotes a potential outlier)

Group 1:	Group 2:	Group 3:	Group 4:
25BW15 F8801 344 25BW15 F8801 282 25BW15 F8806 902 25BW15 WD3481 3of4 25BW15 WD3481 2of4* 25SY31 H3 94160173 25SY31 H3 94031016* 25SY31 H3 94114017* 25SY31 H3 94158165*	25BW15 F8801 332 25BW15 F8801 327 25BW15 F8801 326 25BW15 F8802 490* 25BW15 F8806 918 25BW15 F8806 882 25BW15 F8806 872* 25BW15 WD3481 4of4 25BW15 WD3481 1of4* 25BW15 F8701 131 28 25BW15 F8707 236 25 25BW15 F8707 236 29 25BW15 F8707 236 40*	25BW15 F8801 292	25BW15 F8802 491

Group 1:

The sherds present in the first group include all four of the sherds from the Patterson site (25SY31 H3) along with five sherds from the McIntosh site (25BW15), including two of the four pieces from the Wales Donation (pieces 2 and 3 of 4). This means a total of nine sherds of the thirty sherds are included in the 1st group (Figure 9). The samples in the group all have the same peak locations and combinations. The samples from McIntosh include F8801 344, F8801 282, F8806 902, Wales Donation 3481's 3 of 4 and 2 of 4. Patterson's 94160173, 94031016, 94114017 and 94158165 are the samples present here.

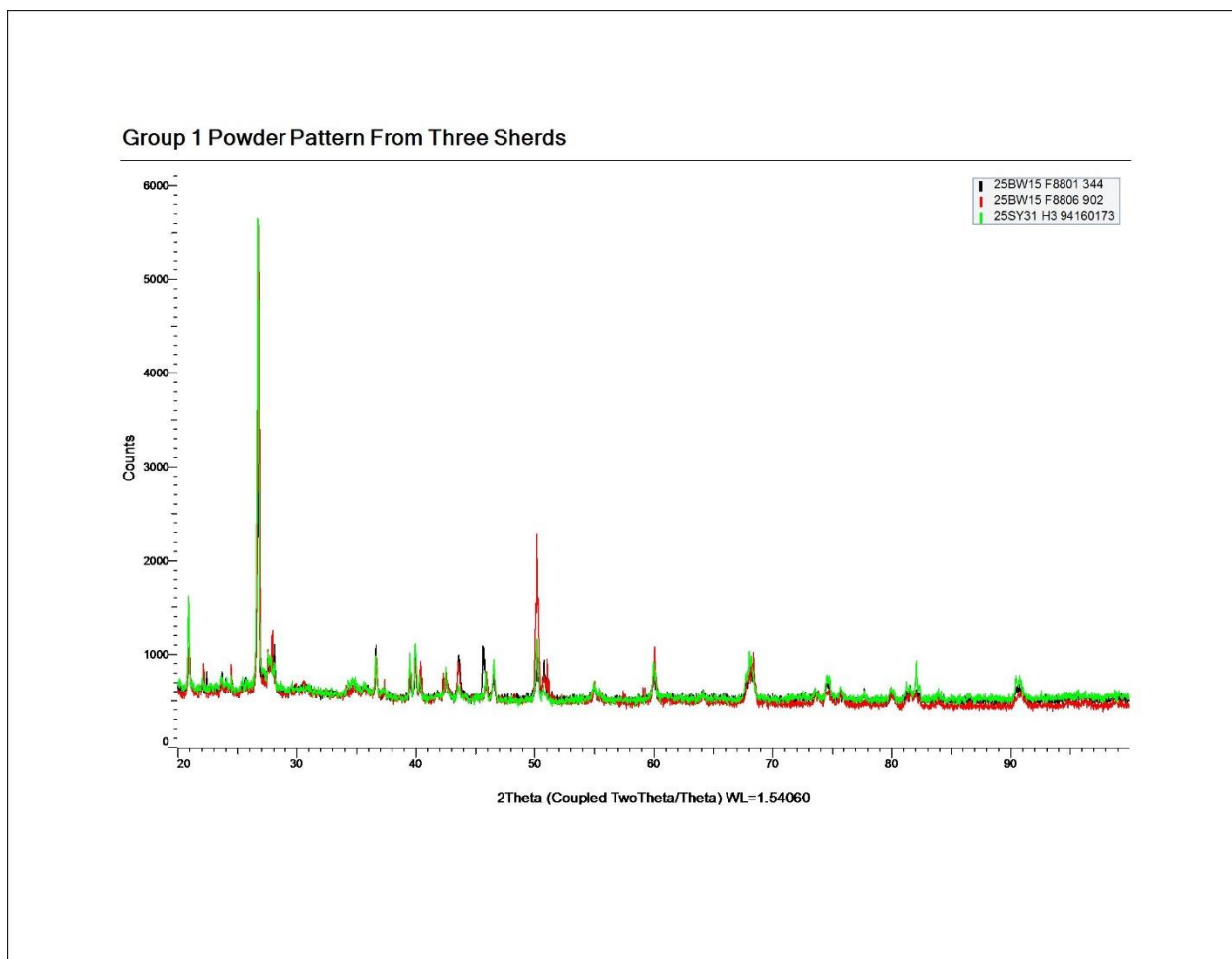


Figure 3.9: Group 1 Powder Pattern

Several outliers have very slight differences in their powder pattern that are difficult to detect, either due to low peak intensity or a very slight peak shift. These samples include 25SY31 H3 94158165 (Patterson). This sherd has a slight difference in the peak pattern at 2θ values 81.4° , with an additional peak as well as a slight peak shift at 46.7° (possible shift from 46.5°). It is also the only sample that shows this particular feature. Additionally, there are two more samples that have a similar difference in the powder pattern variation, 25SY31 H3 94031016 and 25SY31 H3 94114017, both are Patterson site samples. These sherds showed a slight variation in the 2θ values with a potential peak shift at 28.06° (possible shift from 27.7°) and a slight peak shift at 36.6° (a shift from 36.8°). Finally, there is an additional sherd that shows slight variation,

25BW15 from the Wales Donation 3481 artifact 2 of 4. This sample shows variation in the powder at 2Θ 50.3° and 50.45° in the intensity of the peaks located there (Figure 10). These slight differences may indicate a different 3-dimensional structure is involved in the material or mineral that these peaks represent, which would indicate a different characteristic of the clay involved in these sherds than the other sherds to constitute the first group.

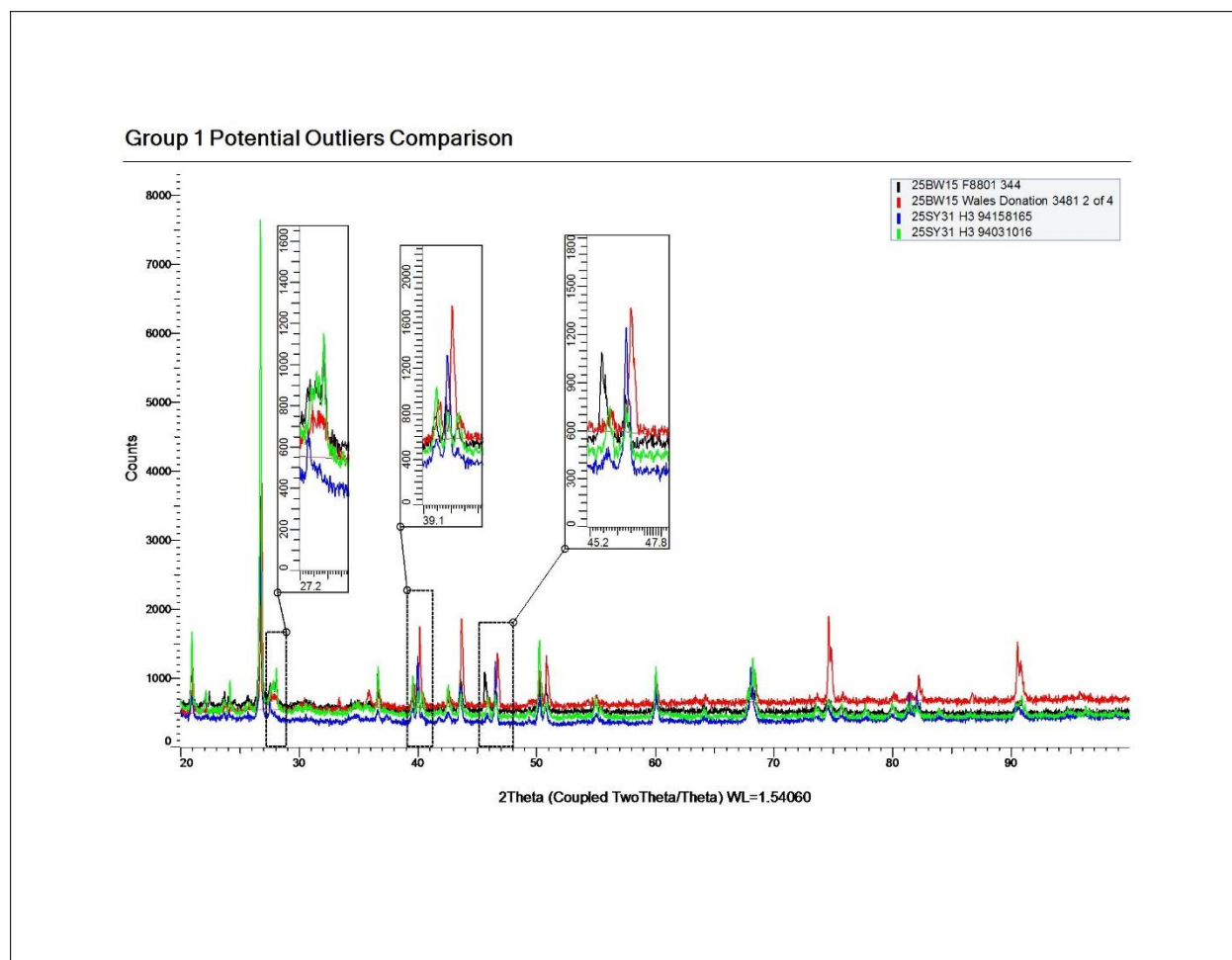


Figure 3.10: Group 1 Potential Outliers Compared to Representative Sample of Group 1 (Black; 25BW15 F8801 344)

All the sherds in Group 1 are body sherds, both at McIntosh and Patterson, and all of the McIntosh sherds look very similar in terms of color, not including samples that showed evidence of being burnt. The sherds from Patterson, however, look very different.

One sherd (25SY31 H3 94158165) was a light brown color with a very friable fabric. Another (25SY31 H3 94160173) was almost black in color, and very hard, making sample collection difficult. These differences could be owed to a number of factors, including the temper material used in their construction, the process by which they were fired and originally created, the temperature they were fired to, etc. As mentioned in the discussion on Patterson, this site showed evidence of a fire, and that too may have contributed to the coloration of the Patterson site sherds and hardness. See Appendix C for images of the sherds.

Group 2:

The sherds in the second group are the most numerous of the sherds currently scanned, containing a total of thirteen samples, all from the McIntosh site. These samples showed variation in their powder pattern as compared to the first group with a peak deletion at 2θ values 29.6° , a peak addition at 35.5° and a peak shift and deletion in the 50° to 50.6° range (Figure 11). The remainder of the Wales Donation artifacts are grouped here, with a potential of two outlier groups. As with the first group, all the samples present in this group have extremely similar powder patterns, with the outliers having slight variations in the form of difficult to detect peak shifts and deletions.

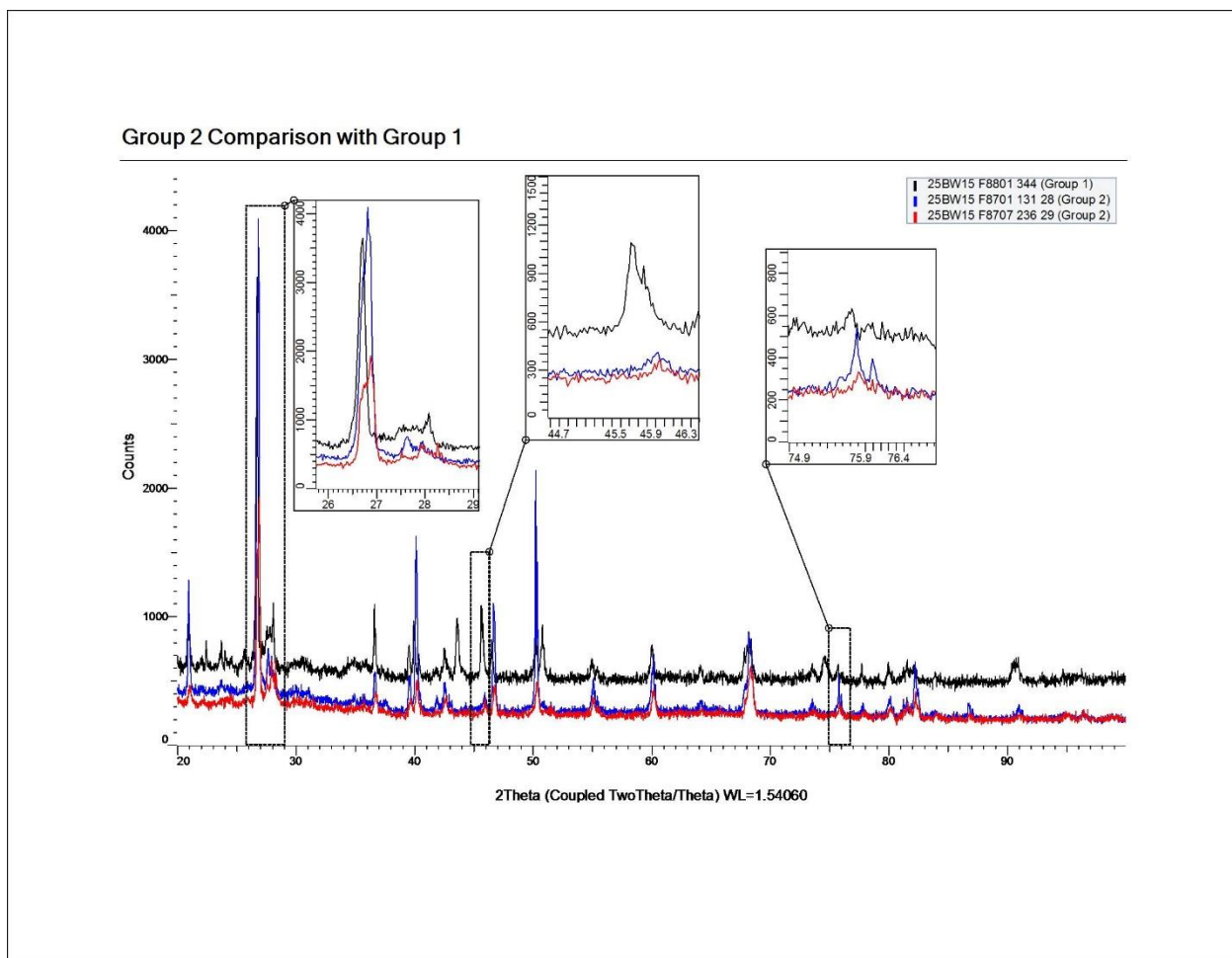


Figure 3.11: Group 2 Representative Samples Compared to Group 1 (Black; 25BW15 F8801 344)

The first of the outliers for the second group contains 25BW15 F8802 490, F8806 872 and Wales Donation 3481's artifact 1 of 4. These sherds all show the same slight powder pattern variation at 2Θ 33.9° and 26.2° with peak additions or shift. Additionally, 25BW15 F8707 236 40 shows a potential peak shift at 2Θ value 41.9° and peak addition at 98.6° (Figure 12). Thus, there are a potential two outlier groups from the second group for a current total of seven potential characteristic powder pattern "fingerprints" of the clays present in these ceramic artifacts.

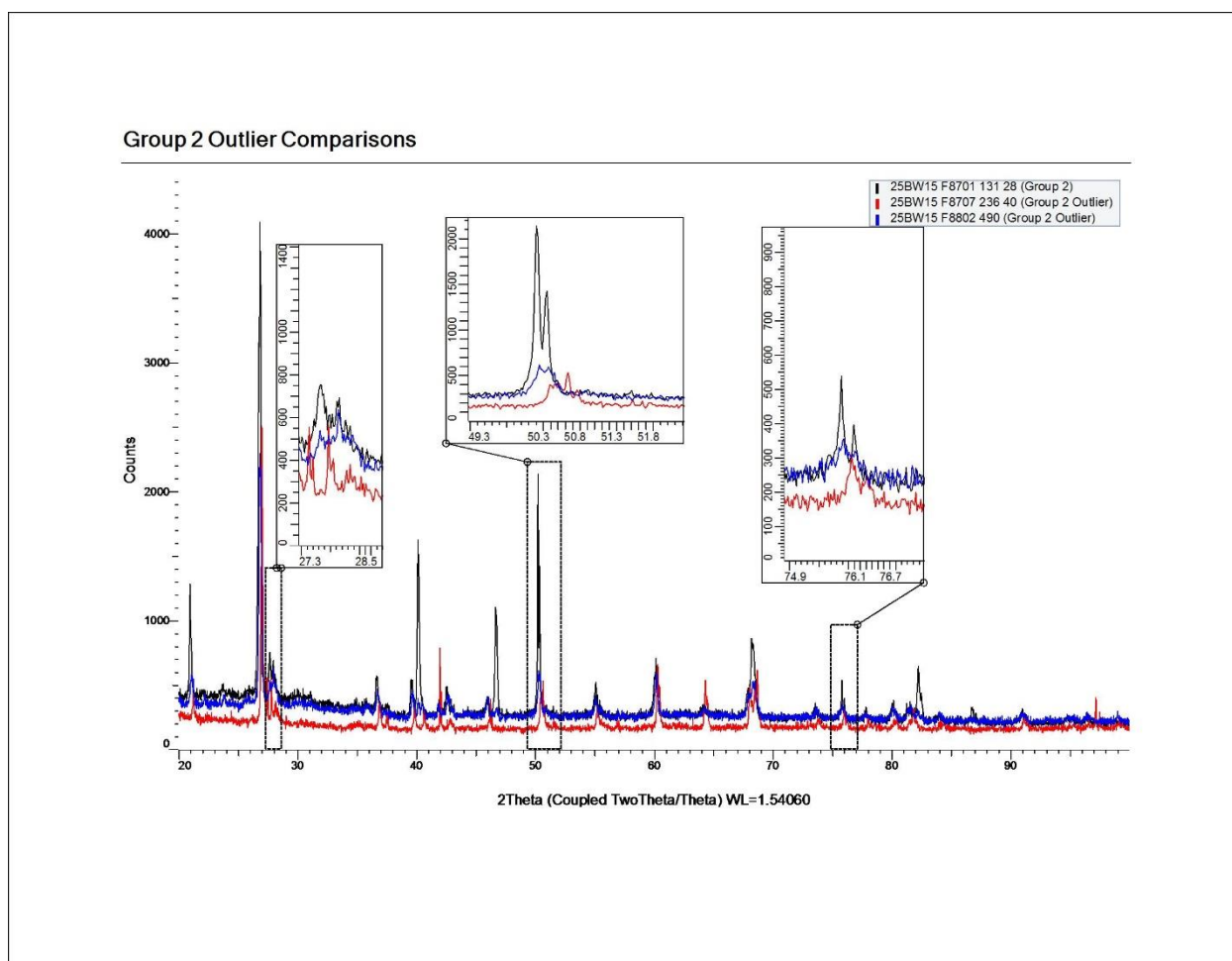


Figure 3.12: Group 2 Potential Differences compared to Group 2 Representative Sample (Black; 25BW15 F8701 131 28)

The McIntosh sherds present in Group 2 are very similar in both design, pre-analysis color and that all were body sherds. When looking at the sample color at 900°C, while it is difficult to tell, it would appear these samples are, in general, a brighter orange color than their Group 1 counterparts.

Group 3 and 4:

Groups 3 and 4 each only contain a single sherd, however the powder patterns of these two sherds show variation significant enough to be considered their own separate groups. Both sherds are from McIntosh: 25BW15 F8801 292 for the third (Figure 13) and 25BW15 F8802 491 for fourth group (Figure 13) are sherds that showed the greatest

variation when compared to the first and second groups. 25BW 15F8801 292 (Group 3) showed variation with additional peaks at 2θ values 78.7° and 78.99° as well as a double peak from 86.7° to 87° . 25BW15 F8802 491 (Group 4) showed additional peaks in the powder pattern at 2θ values 64.8° and 65° with a potential third peak at the 45.3° value.

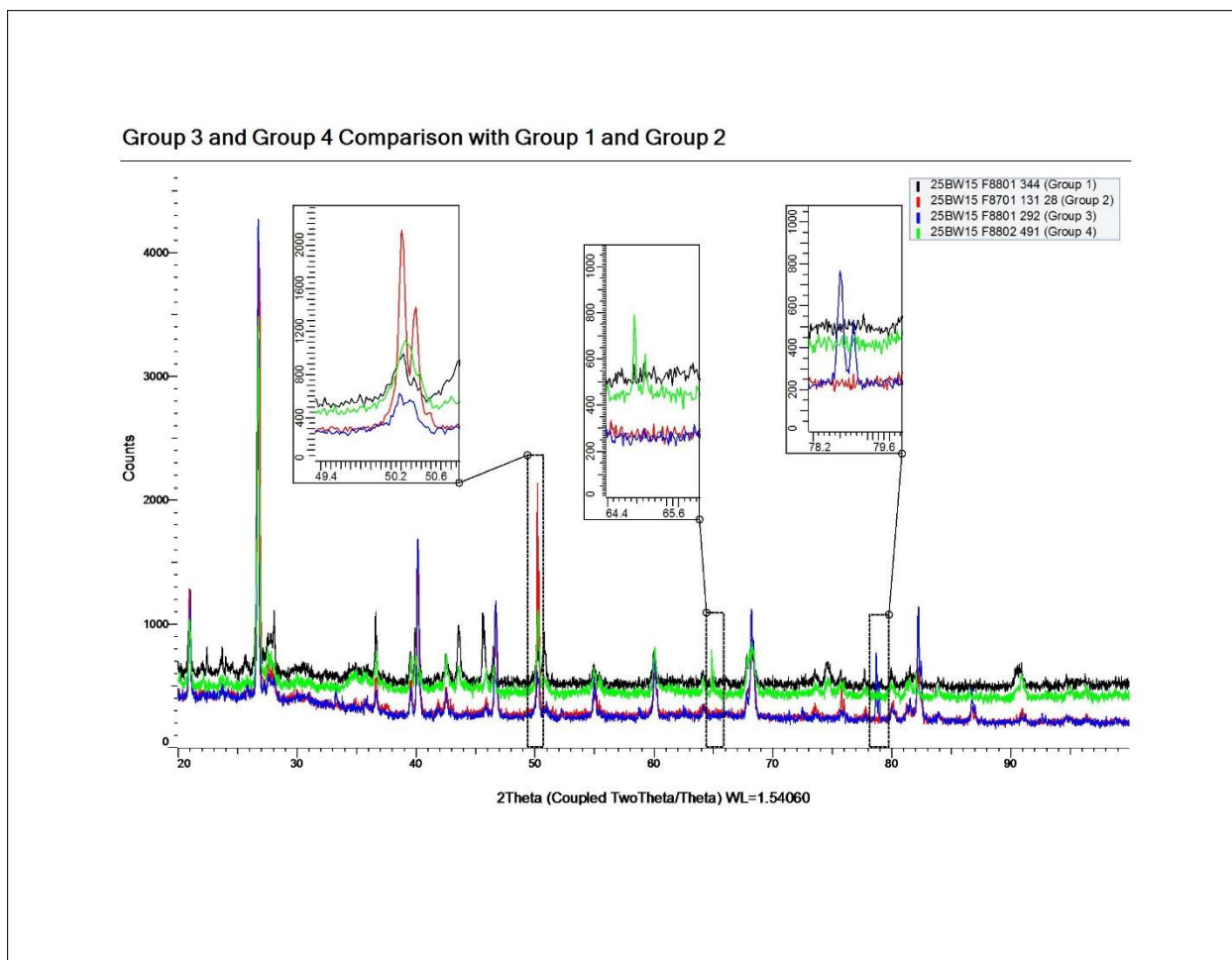


Figure 3.13: Group 3 (Blue; 25BW15 F8801 292) and Group 4 (Green; 25BW15 F8802 491) compared to Representative Samples from Group 1 (Black; 25BW15 F8801 344) and Group 2 (Red; 25BW15 F8701 131)

Discussion and Conclusion:

The results of this initial study allow several conclusions. First, X-Ray Diffraction is able to discern the characteristic “fingerprints” of various clays used in the production of the ceramic vessels. At the very minimum, there appear to be four clays or clay recipes used in the production of ceramics found at the McIntosh site. As an intra-site analysis,

even with a small scale sampling reported on here, it is interesting that there is as much variation found here. As mentioned by Koch (1995), the ceramic artifacts found at McIntosh show evidence of Upper Republican and Smokey Hills phase construction. If this is true, the ceramic artifacts here could potentially include clay sources from those regions as well, a possible explanation as to why we see variation in the ceramic clays present in McIntosh's artifacts.

While a number of these ceramics are from the same storage or refuse pit, the powder patterns indicate that vessels with different clays are in use. This indicates that not all the sherds found in an individual feature are from the same vessel. An excellent example of this can be seen with McIntosh Feature 8801. For this case study, a total of seven sherds were scanned with XRD; of these seven sherds two are placed firmly into Group 1, four sherds are in Group 2 and the single sherd comprises Group 3. Though this does not necessarily indicate that the raw sources of the clays came very a great distance away from McIntosh or that the sources themselves are greatly separated by distance themselves, it does indicate that a number of clay sources was used in the production of the ceramic vessels found at the McIntosh site.

While the sample from the Patterson site is small, the samples yielded powder patterns that matched the Group 1 powder pattern. Interestingly, these sherds also matched samples from the McIntosh site with a number of sherds matching the groups from Features 8801, 8806 and two sherds from the Wales Donation (3481) from the McIntosh site. While three of the four sherds from Patterson might be considered outliers from Group 1, their powder patterns require additional research and processing to

determine if they are indeed part of the characteristic Group 1 clay, or if they constitute their own characteristic clay group.

The results of this case study point to the potential of XRD to be able to distinguish among different clay sources or clay recipes, eventually allowing for studies to be conducted towards the goals of sourcing (pinpointing the geographic region the clay or ceramic came from) or characterization (what specific material or mineral is different in the clay of this clay powder pattern group 1 versus group 2) studies.

While this case study has not necessarily shed more light on the debate over CPT population interactions, I believe it has shown that XRD with our methodology developed to incorporate a more non-destructive analysis process can be a useful tool toward that overall goal as I proceed with future research. It showed that the capabilities can not only discern different clay patterns on an intra-site level at the McIntosh site, but that it can also find similarities between sites with a significant distance separating them.

Future Studies:

As this study proceeds forward I will modify the study towards the goal of monitoring clay source movement by building a database; a database of powder patterns of raw clay sources found in the Central Plains area. By building a database of raw clay sources, it is possible to potentially map ceramics and link their origin to a specific geological region and source of where the clay was collected. The emphasis here is collected, as it is shown that while some groups were more permanent in their locations, some groups appeared to be more nomadic, for example those at McIntosh. By building and maintaining a database of powder patterns, anyone who is researching ceramic clay sources in the region using XRD, regardless of the tradition affiliation or time period,

would be able to have a ready database from which to pull potential raw sources. This database could also contain laboratory grade minerals, materials and compositions that are commonly found in clays, to assist with characterization of the clays, i.e. what specifically is present in this clay source that is not present in this clay source.

Characterization results can assist in a more detailed analysis of the clays and help to narrow down the source of the clay, even if it is not a source that has been collected and is present in the database.

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CHAPTER 4: Conclusion

Through the development of a minimally destructive procedure to analyze clay paste from CPt ceramics and the use of new technology available in XRD, I have shown that XRD is able to discern different characteristic powder patterns of different clays found in CPt ceramics. As mentioned in Chapter 3, in the future I will extend this methodology to additional ceramic artifacts found at Patterson and McIntosh, as well as include additional sites from various CPt phases. I will begin to explore why McIntosh may have so many characteristic clay powder patterns by comparing the powder patterns found at McIntosh with powder patterns found in other phases, in particular the Upper Republican and Smokey Hills phases, as it has been mentioned by Koch (1995) that the ceramic assemblages show signs of construction habits from these phases. In addition to adding more ceramic artifacts from additional CPt sites, I plan to begin including raw clay sources into the study as well, and see if it is possible to trace some of these characteristic clay patterns to a specific region or locale. This would further our ability to interpret and map out interactions amongst CPt populations by specifically identifying where the raw clay source came from.

I will also begin working on characterization of specific minerals and materials present in the clay's make-up. This can be achieved by creating our own unique powder

pattern database of research grade minerals and materials and their individual powder patterns and comparing this database to the powder patterns we gain from the ceramics and raw resources. Additionally, by understanding exactly what elements are present will help us narrow down possible candidates for materials and minerals present in the clay. This can be achieved by following X-Ray Fluorescence (XRF) and Neutron Activation Analysis (NAA) methodologies and using the results from these elemental compositional analysis methods and restricting our search parameters to these specific elements for the XRD powder pattern comparison. Furthermore, both XRF and NAA are considered useful sourcing techniques, and their results on the analysis of ceramics can be grouped similarly to how the XRD powder patterns are grouped, and a comparative study between XRD groupings and NAA/XRF groupings could be conducted.

While only a case study, the results are promising and show that there are multitude of future research opportunities that can be conducted into CPt pottery, XRD methodologies for sourcing studies in archaeology and that more research is required to be able to understand the movement and interaction of CPt populations.

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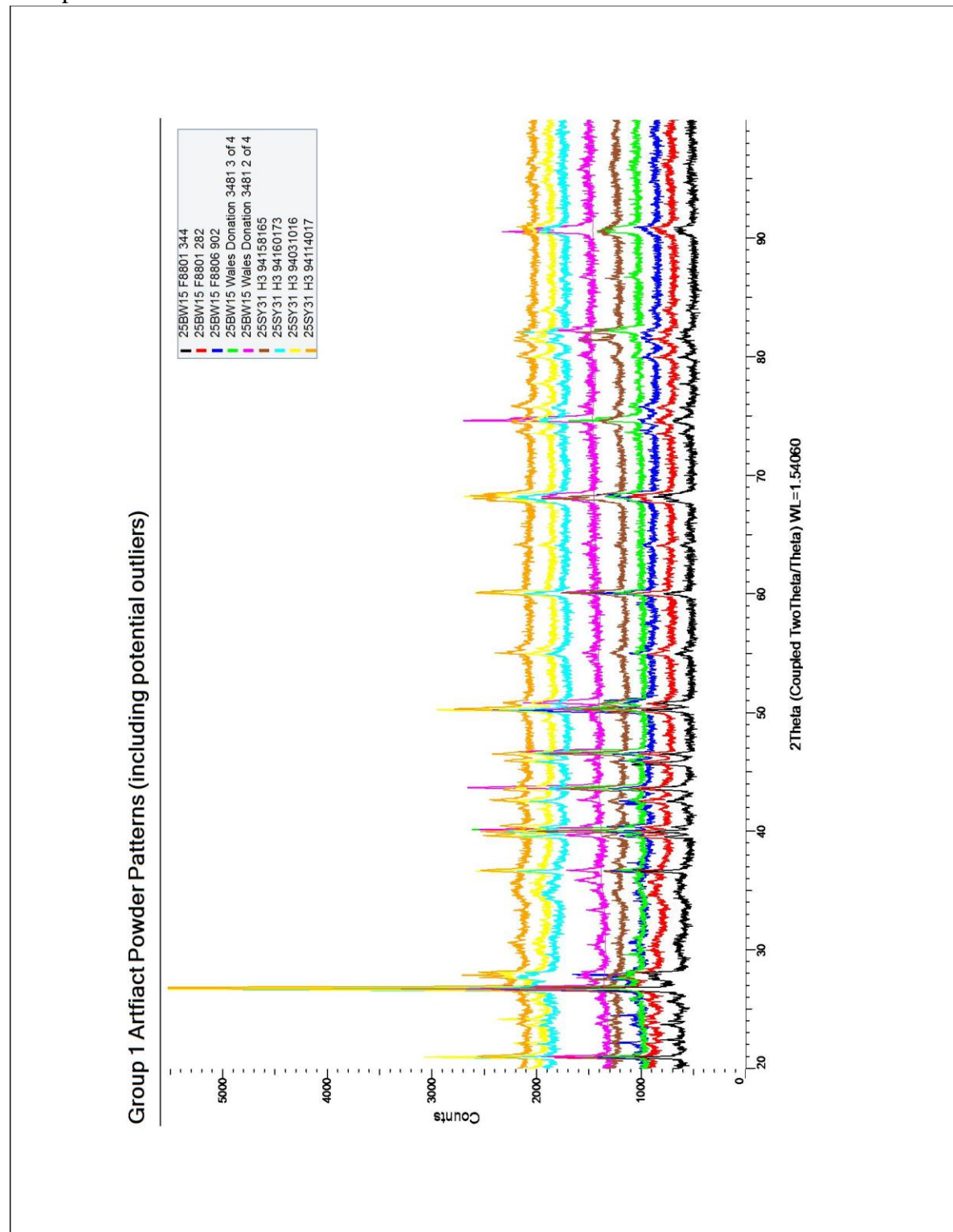
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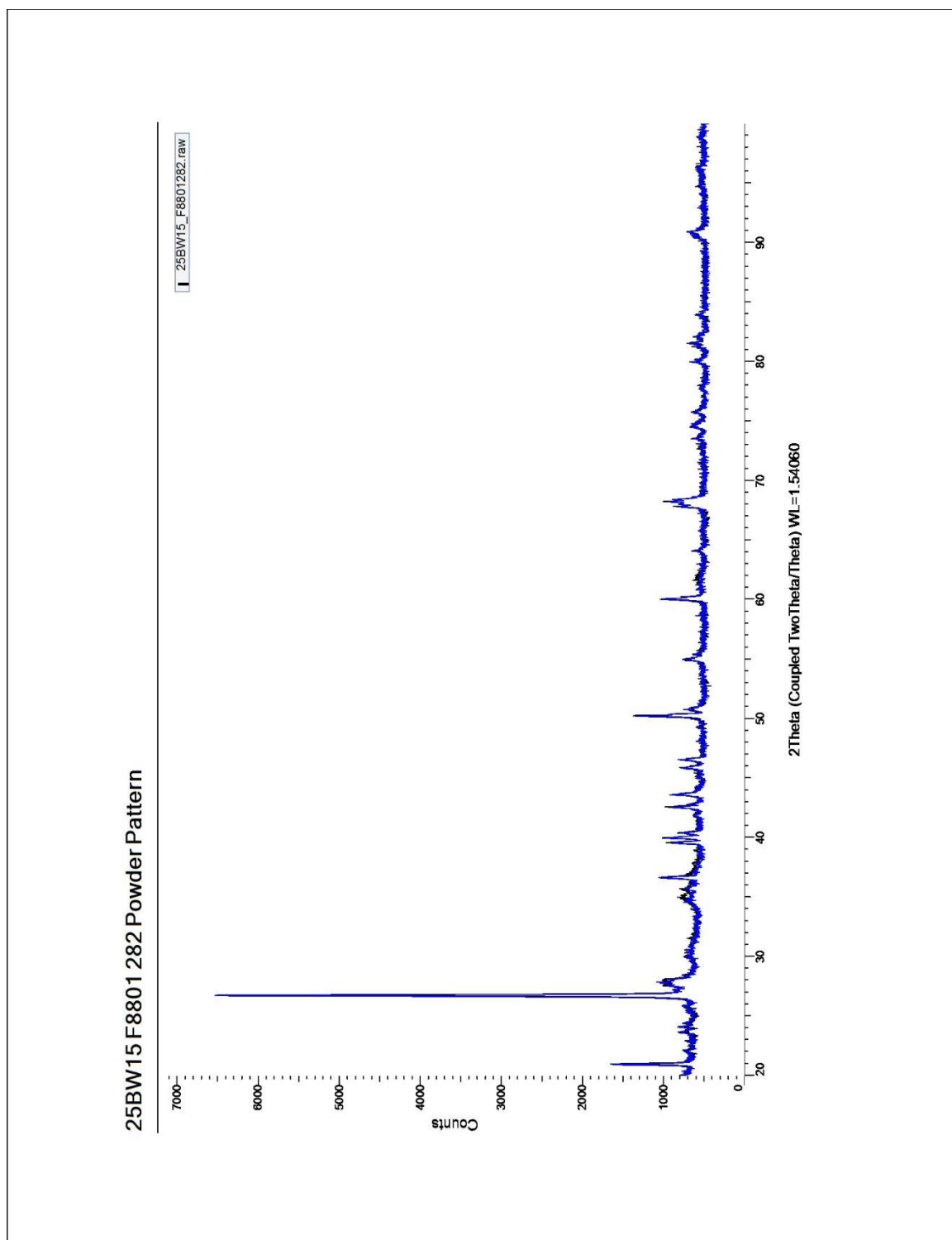
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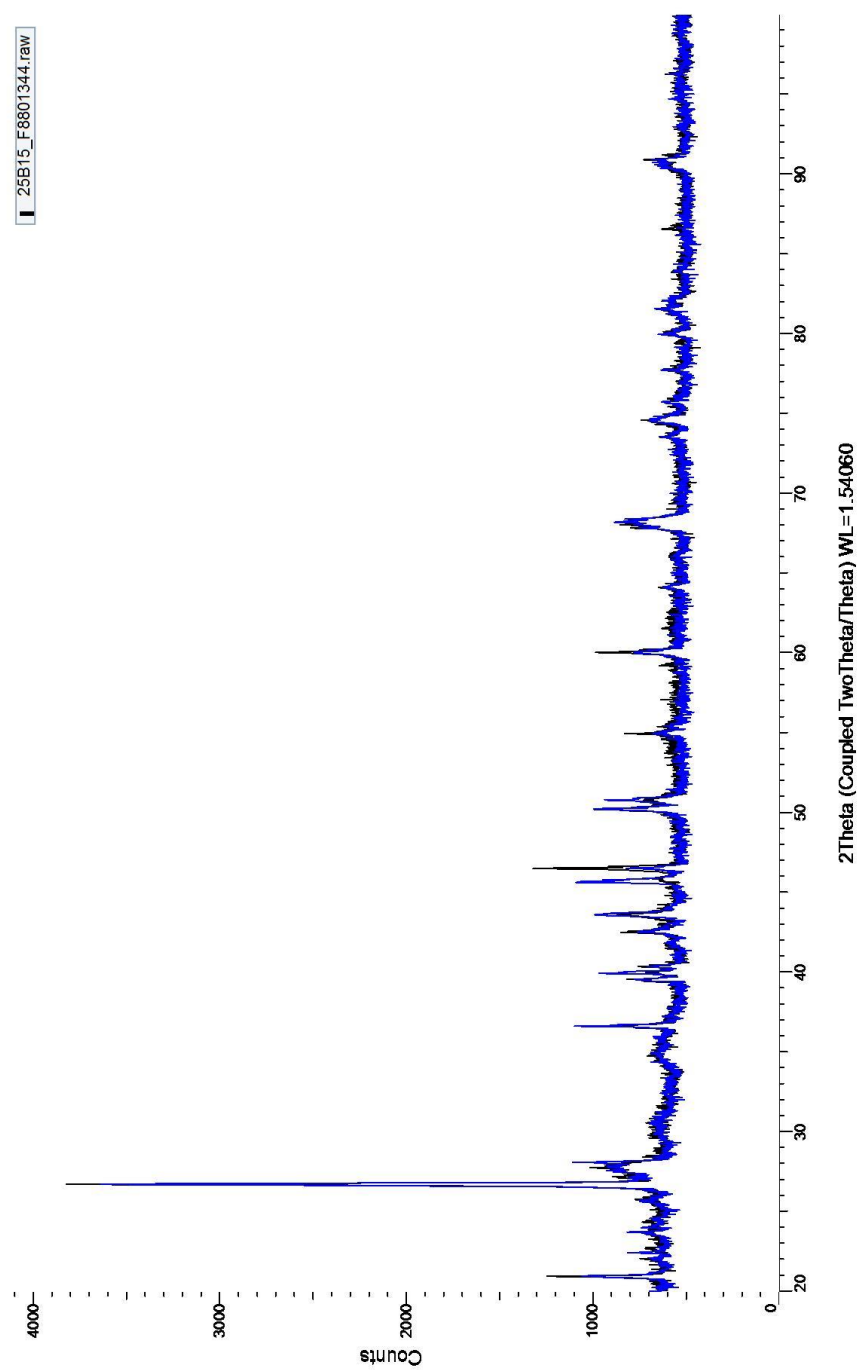
Appendix A: Powder Patterns

Group 1 Powder Patterns:

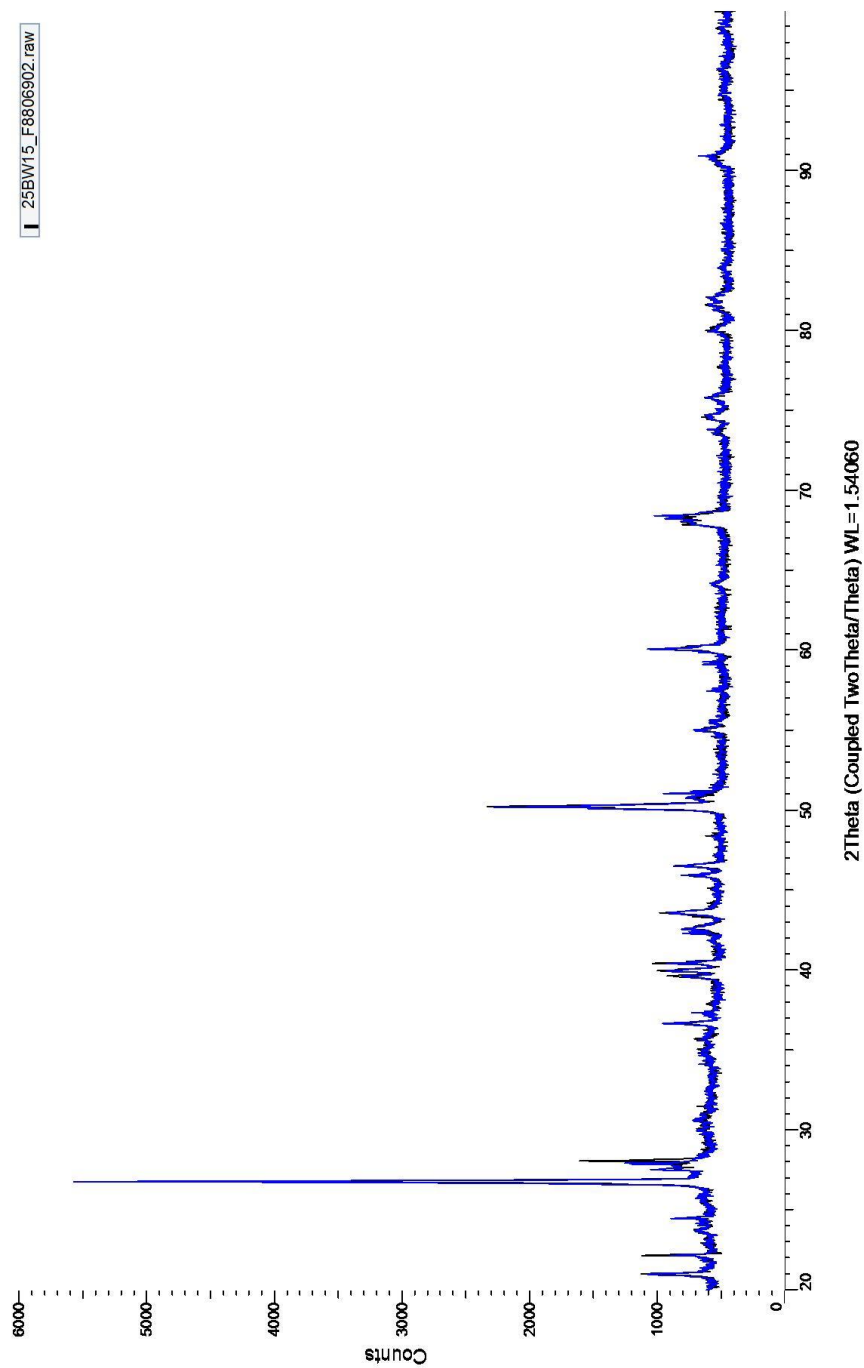




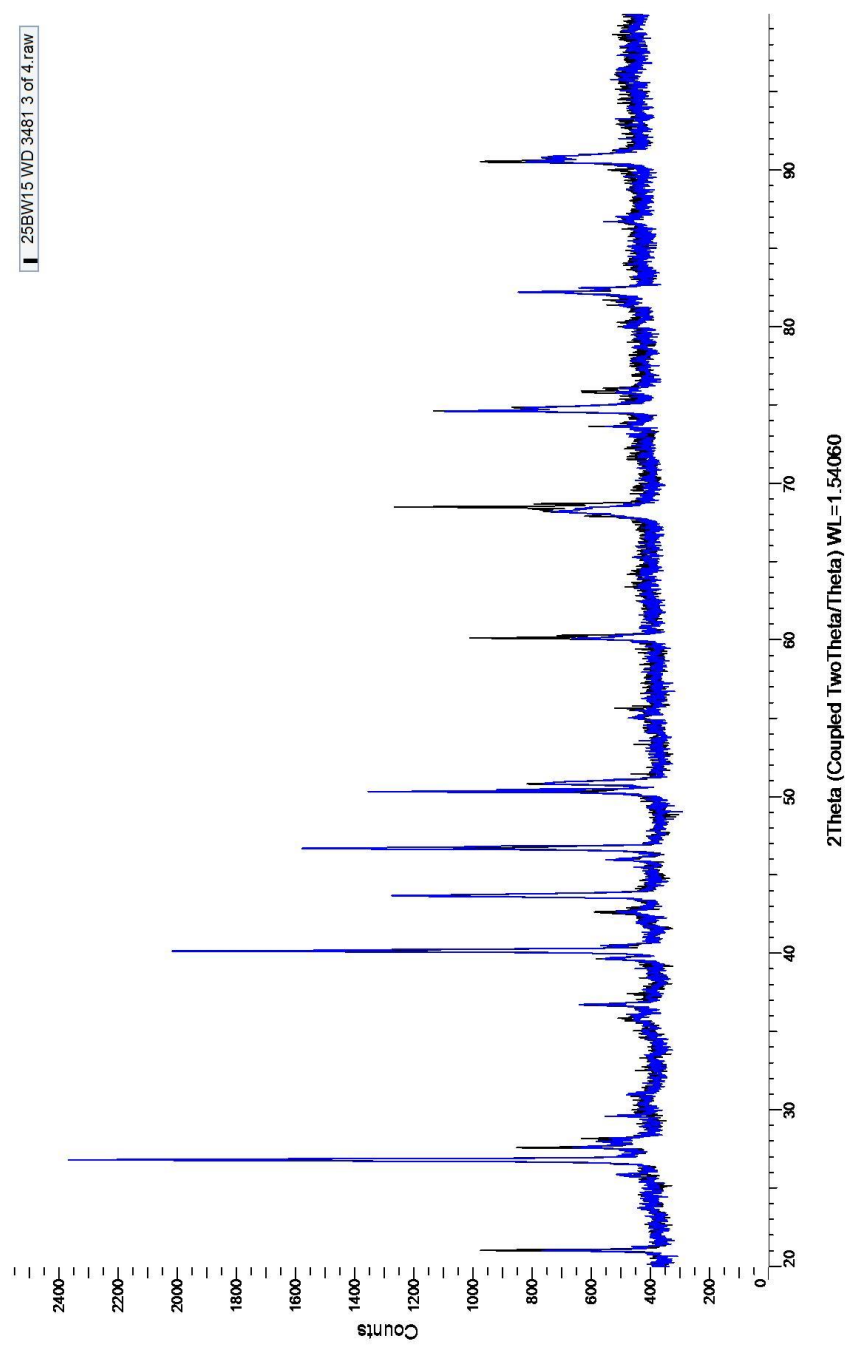
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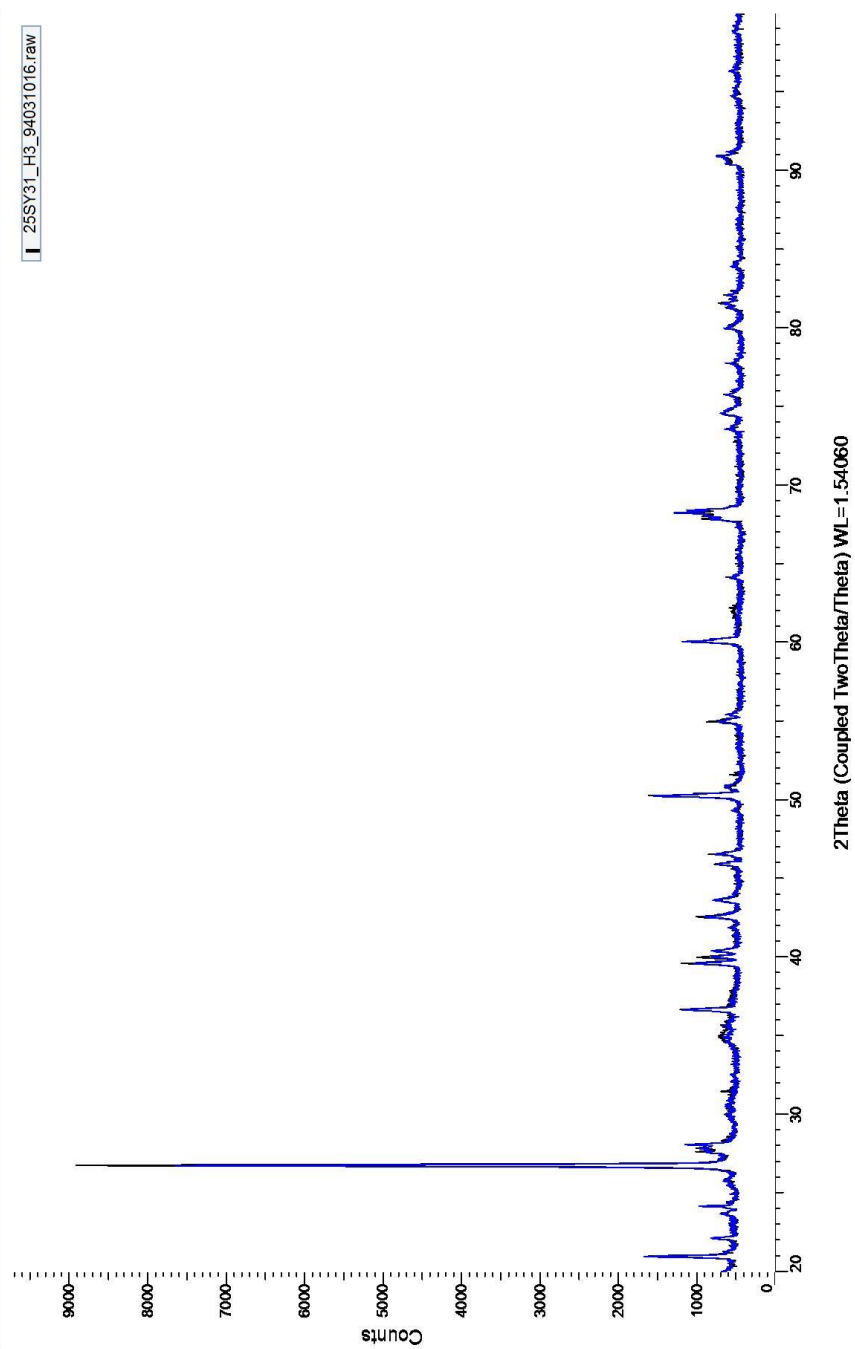
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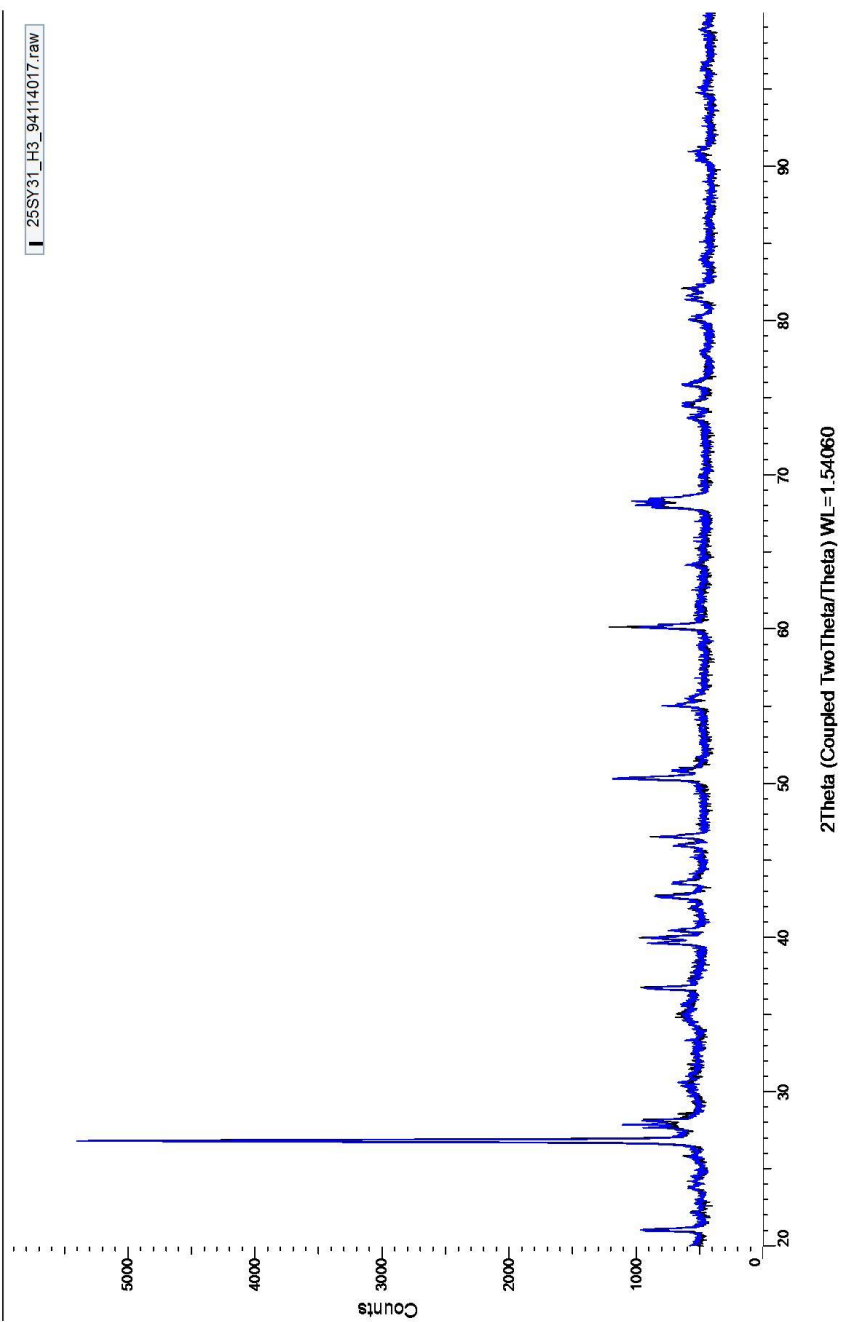
25BW15 Wales Donation 3481 3 of 4 Powder Pattern



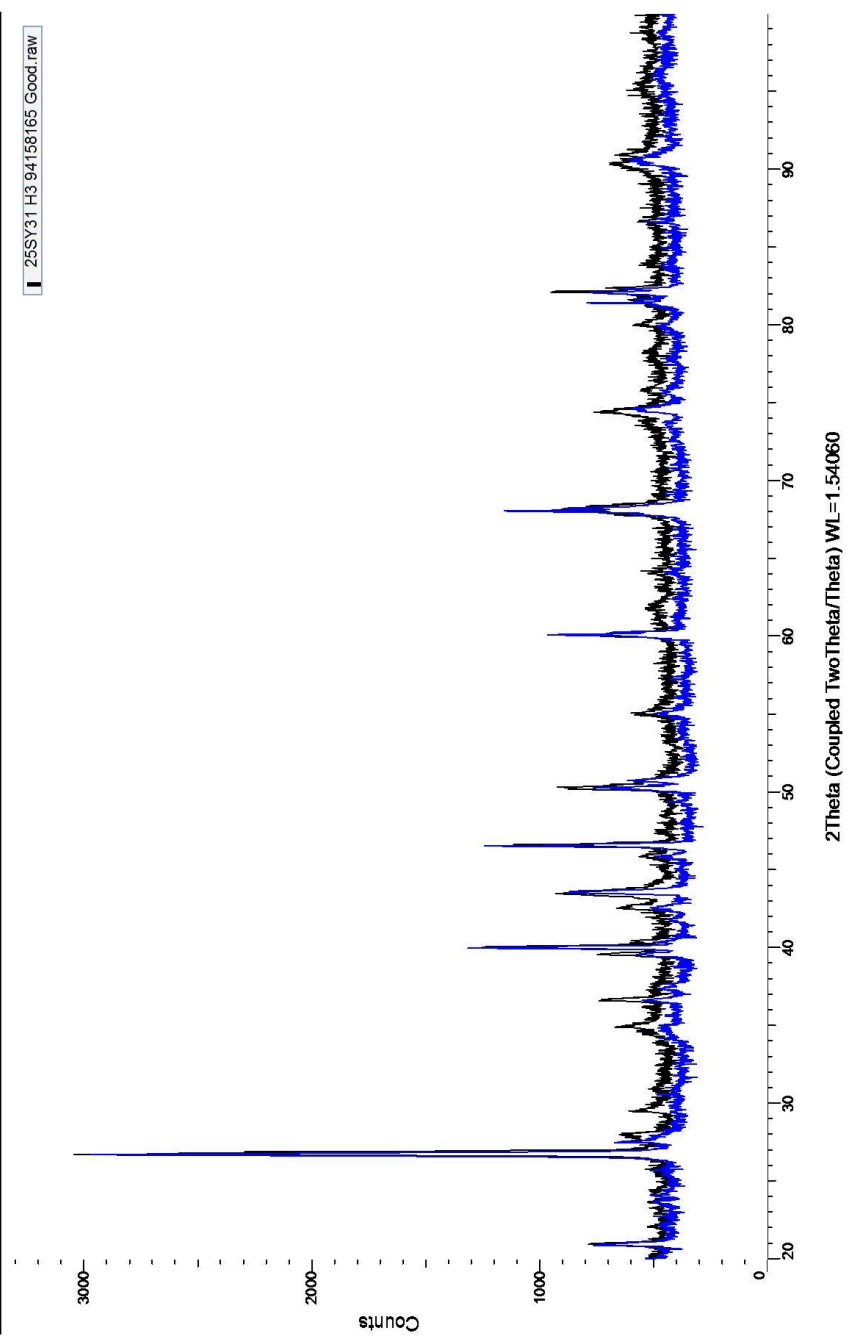
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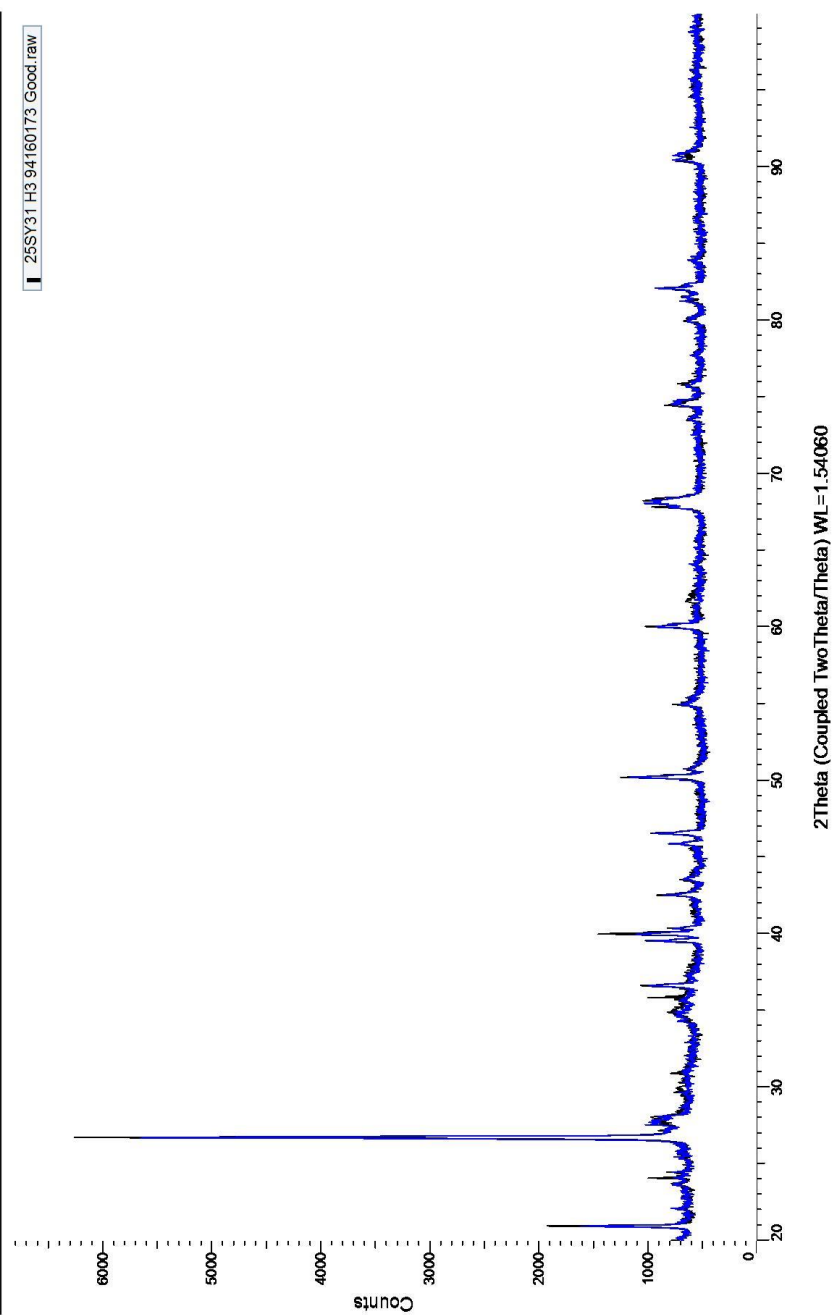
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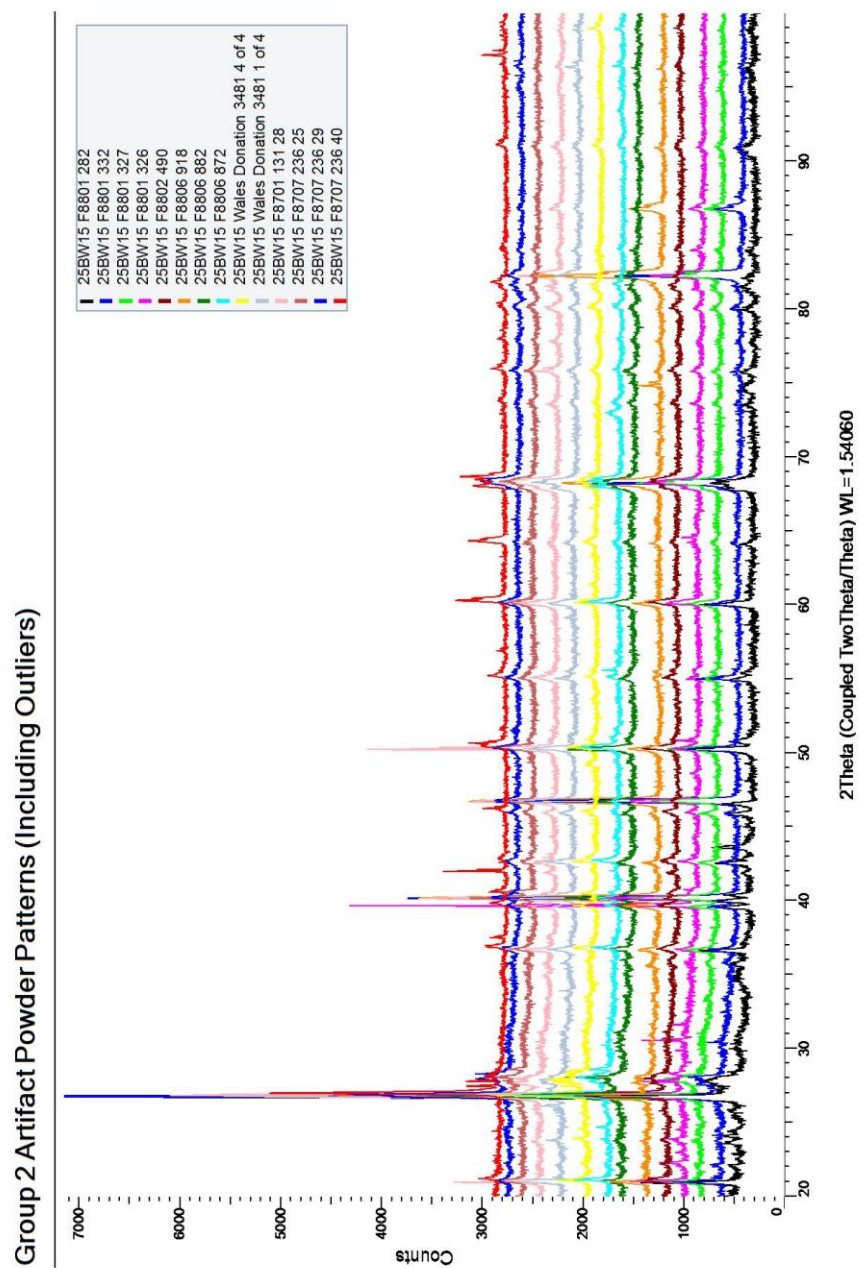
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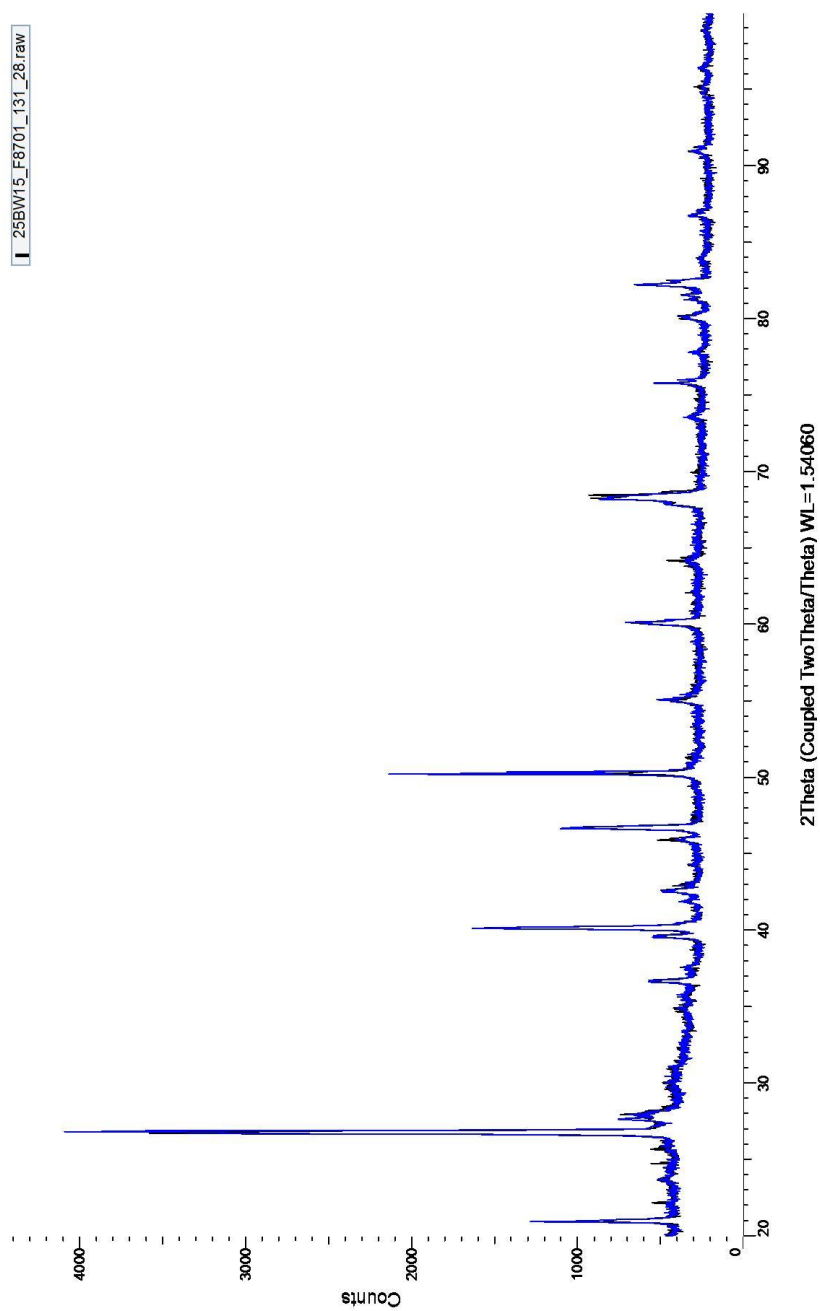
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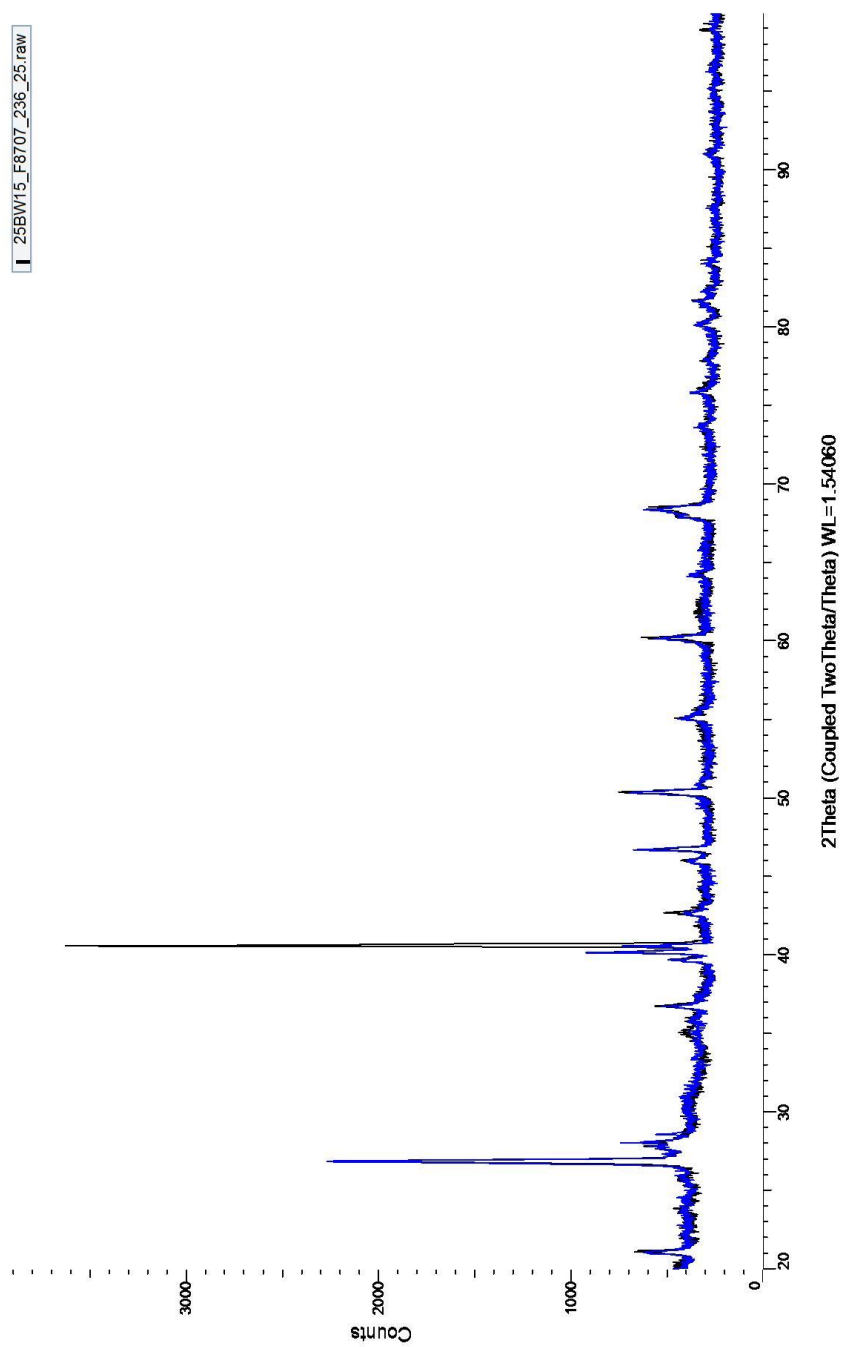
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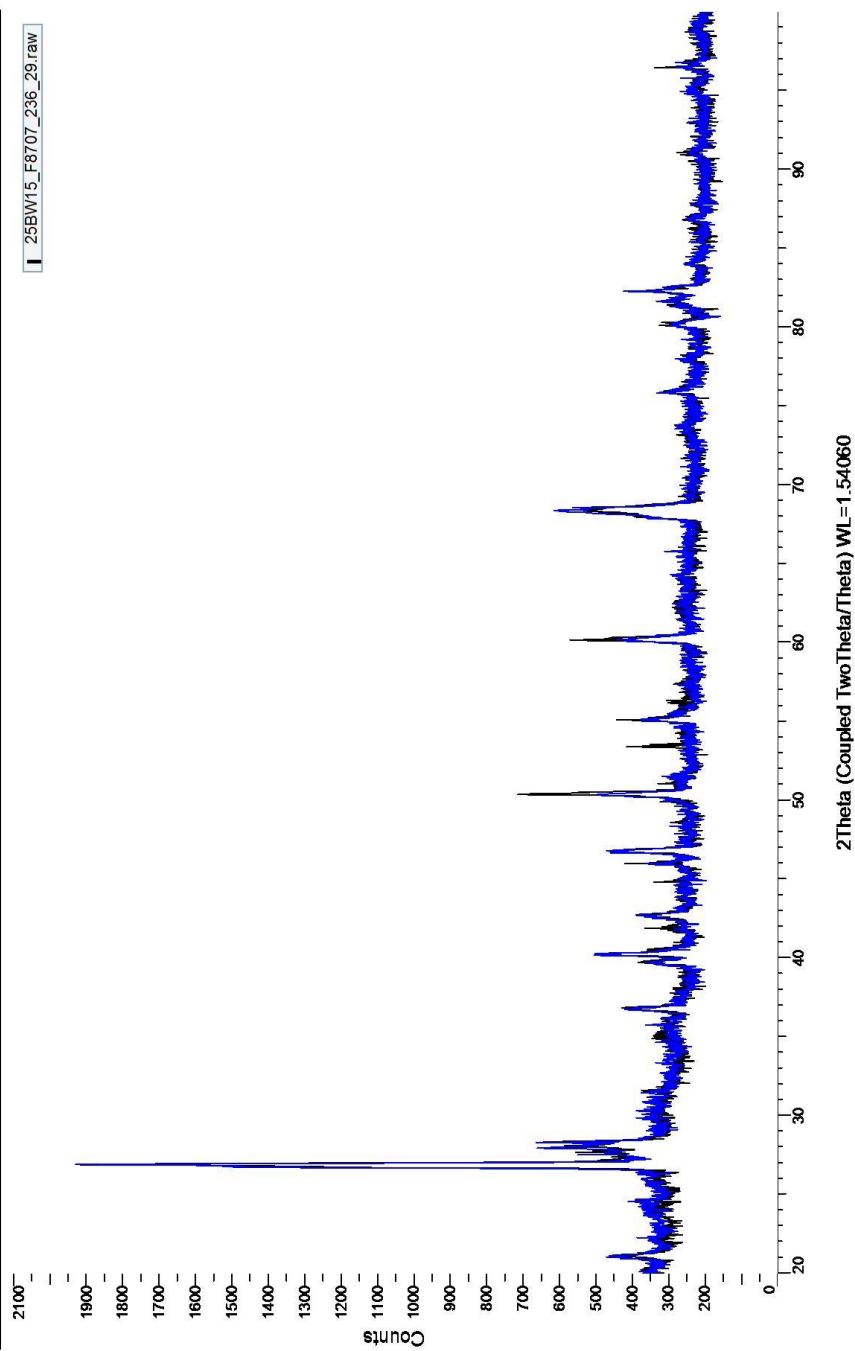
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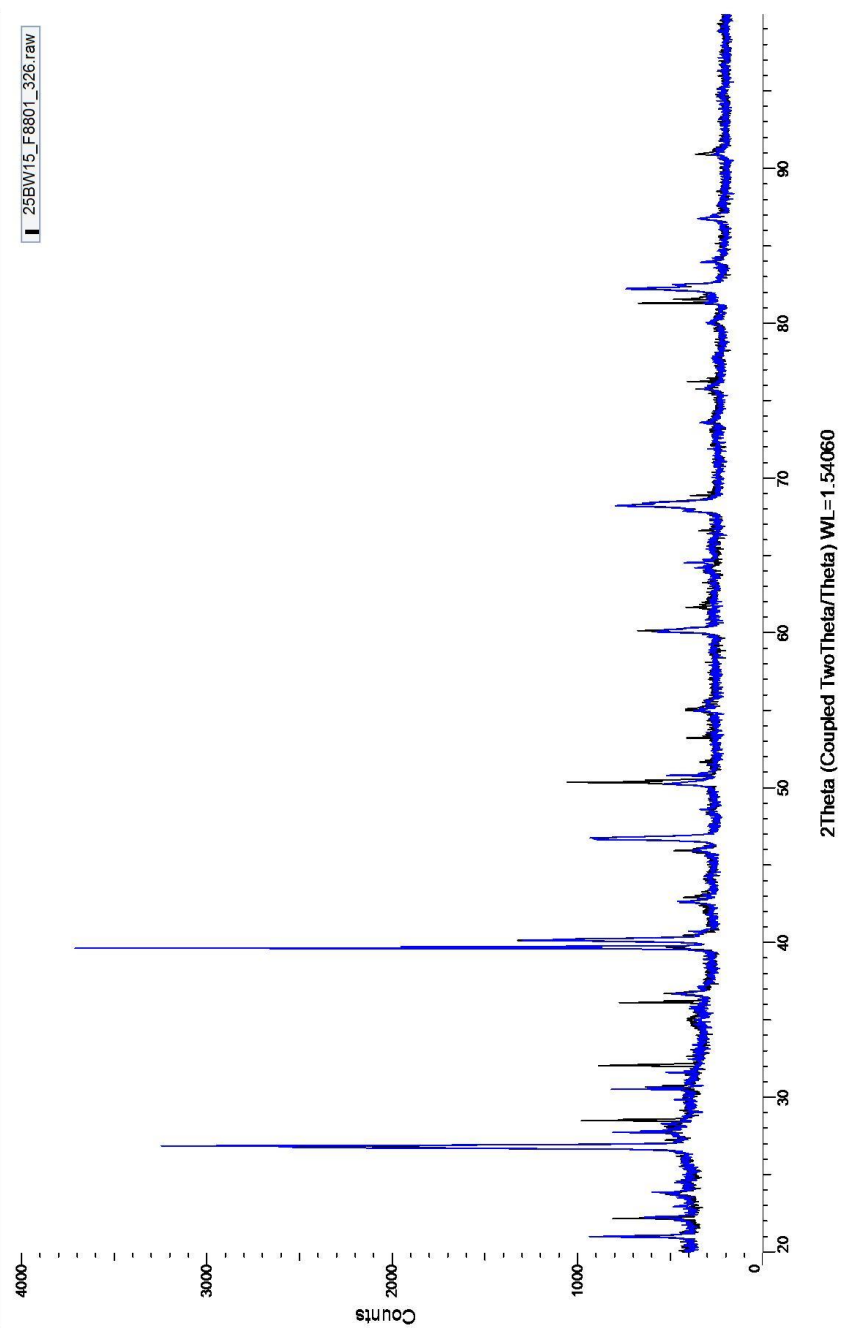
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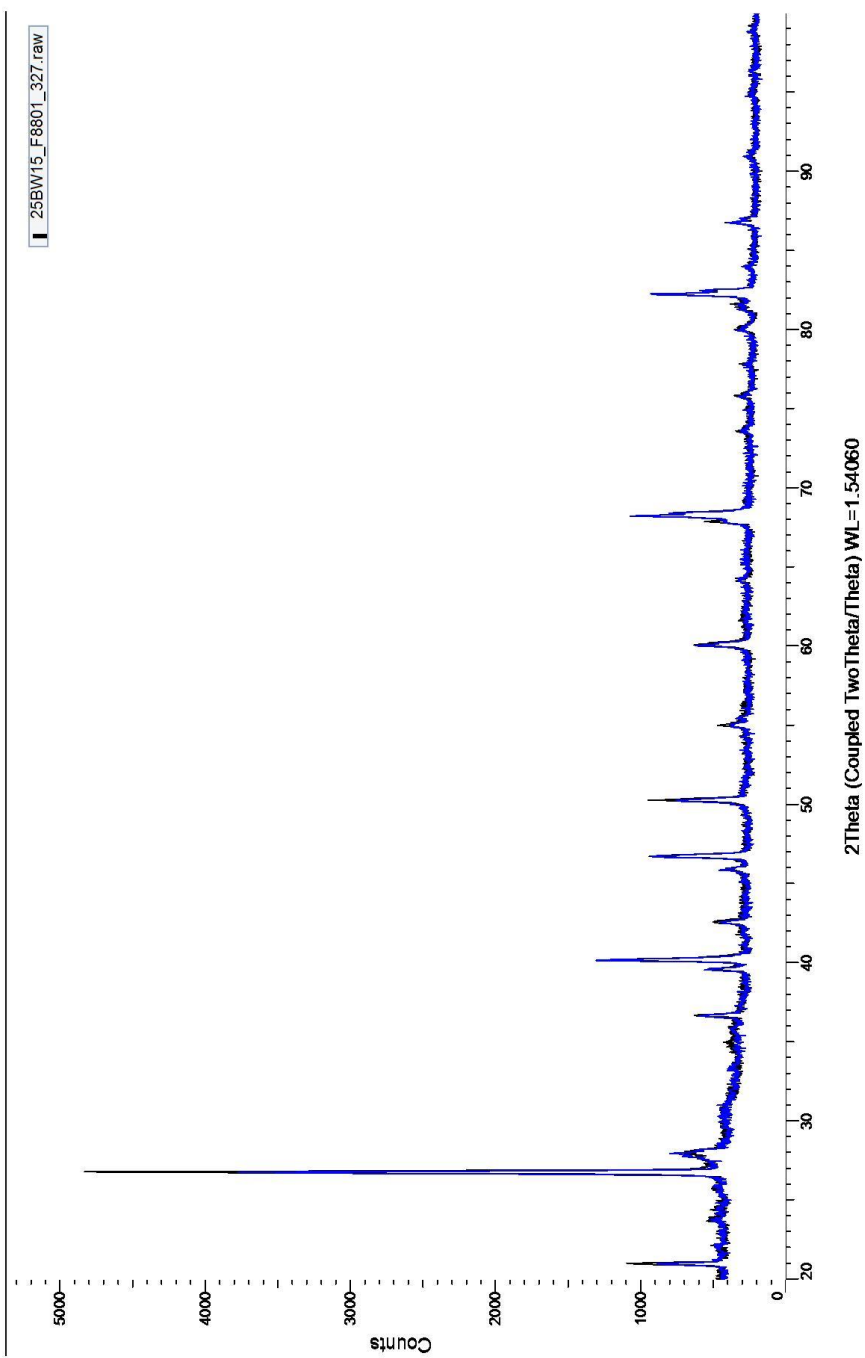
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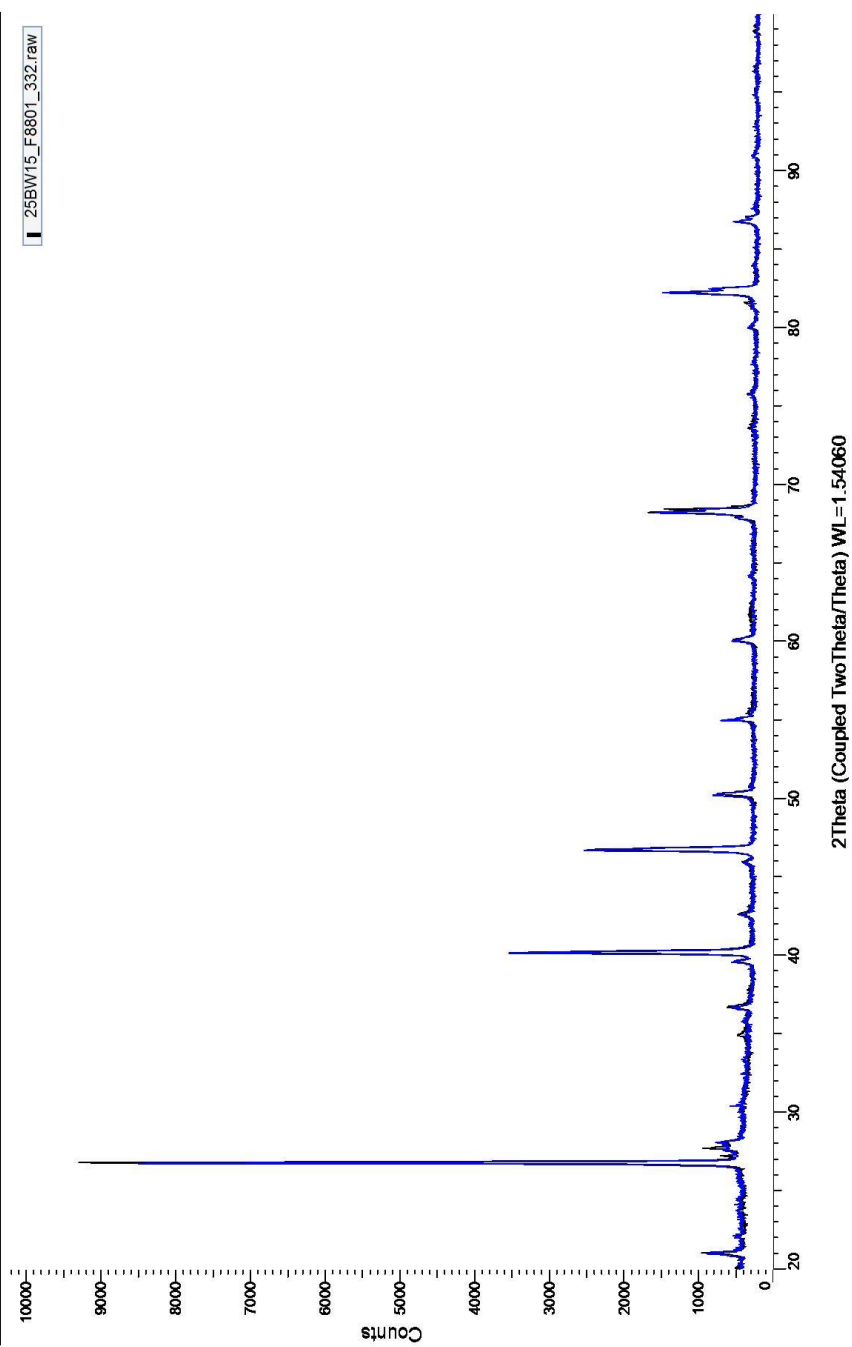
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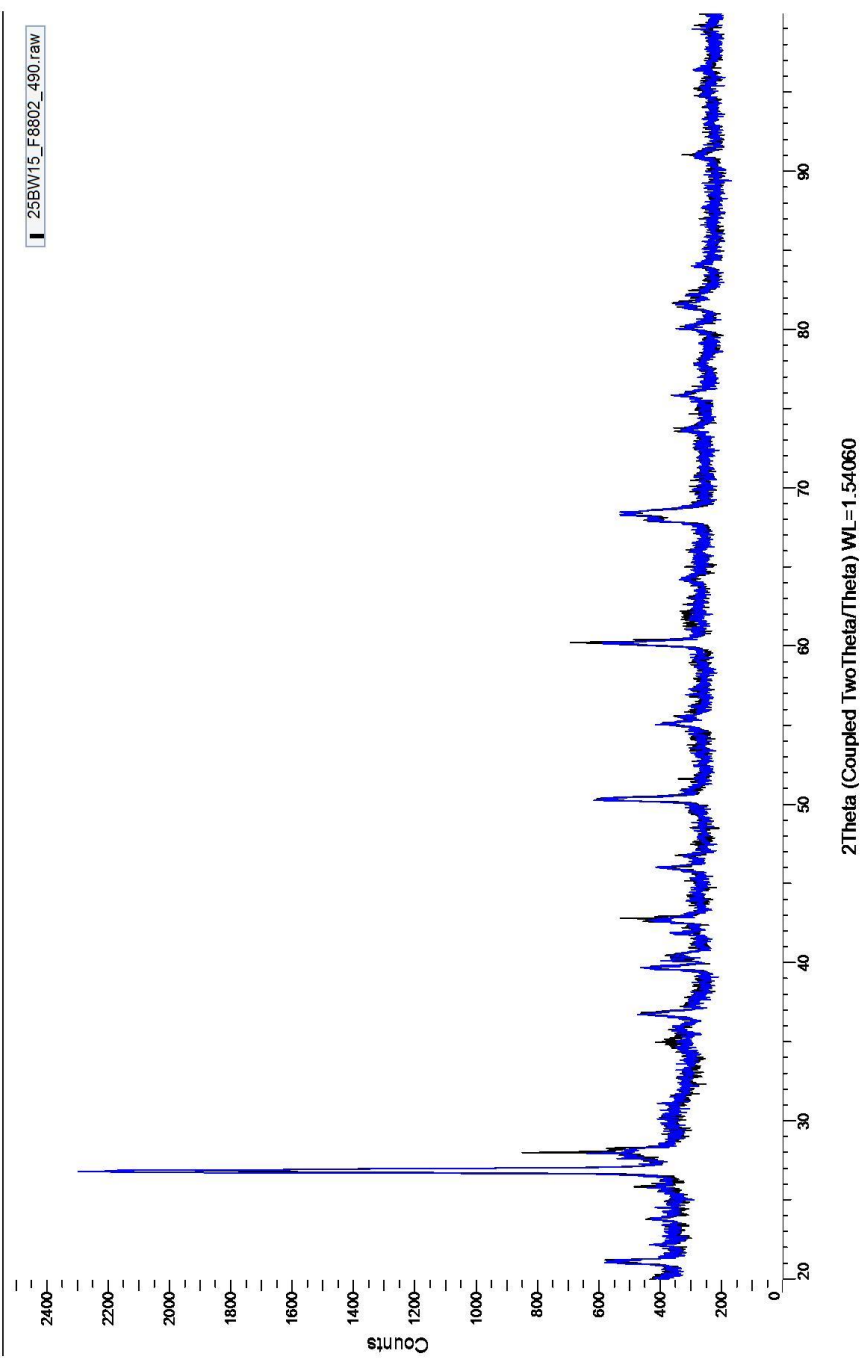
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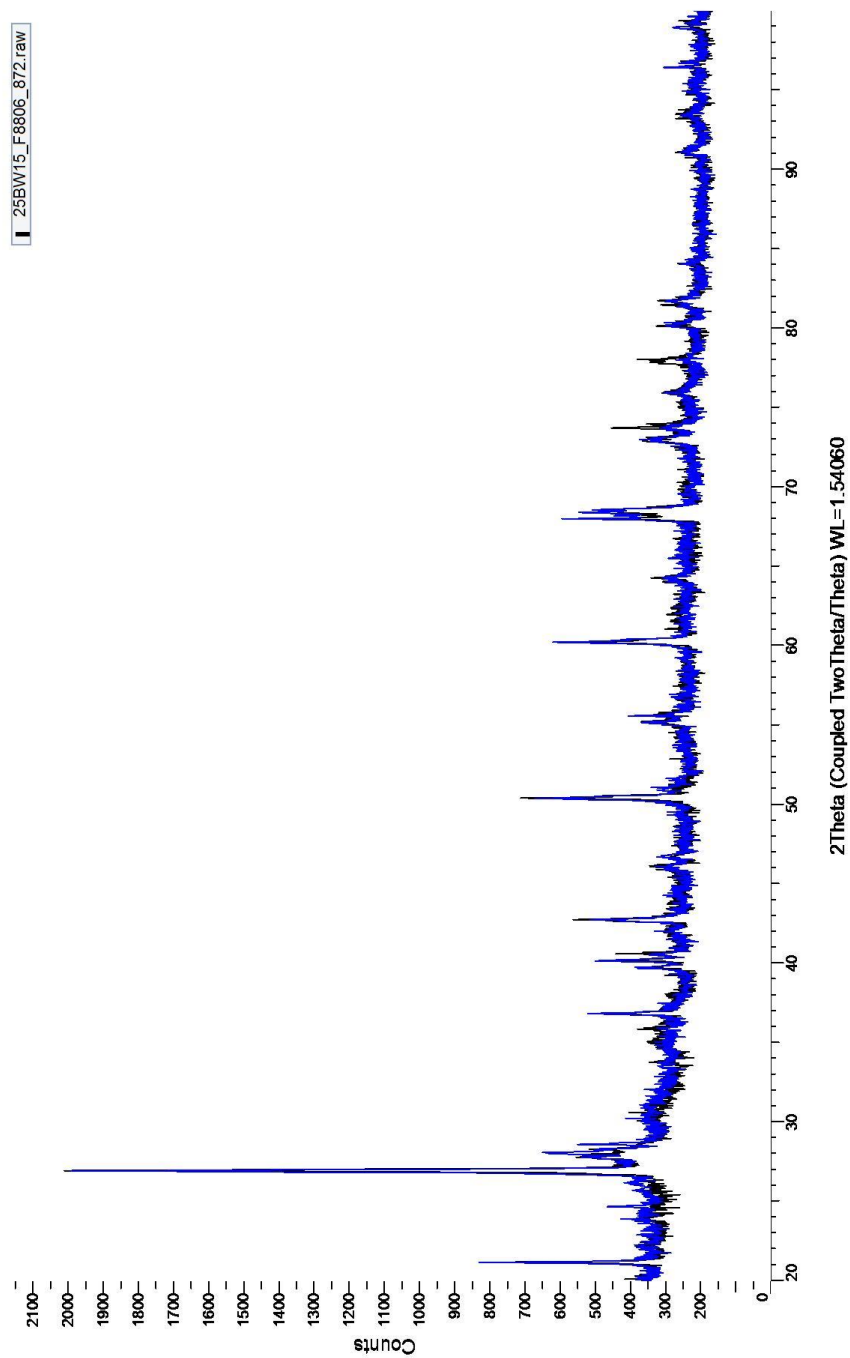
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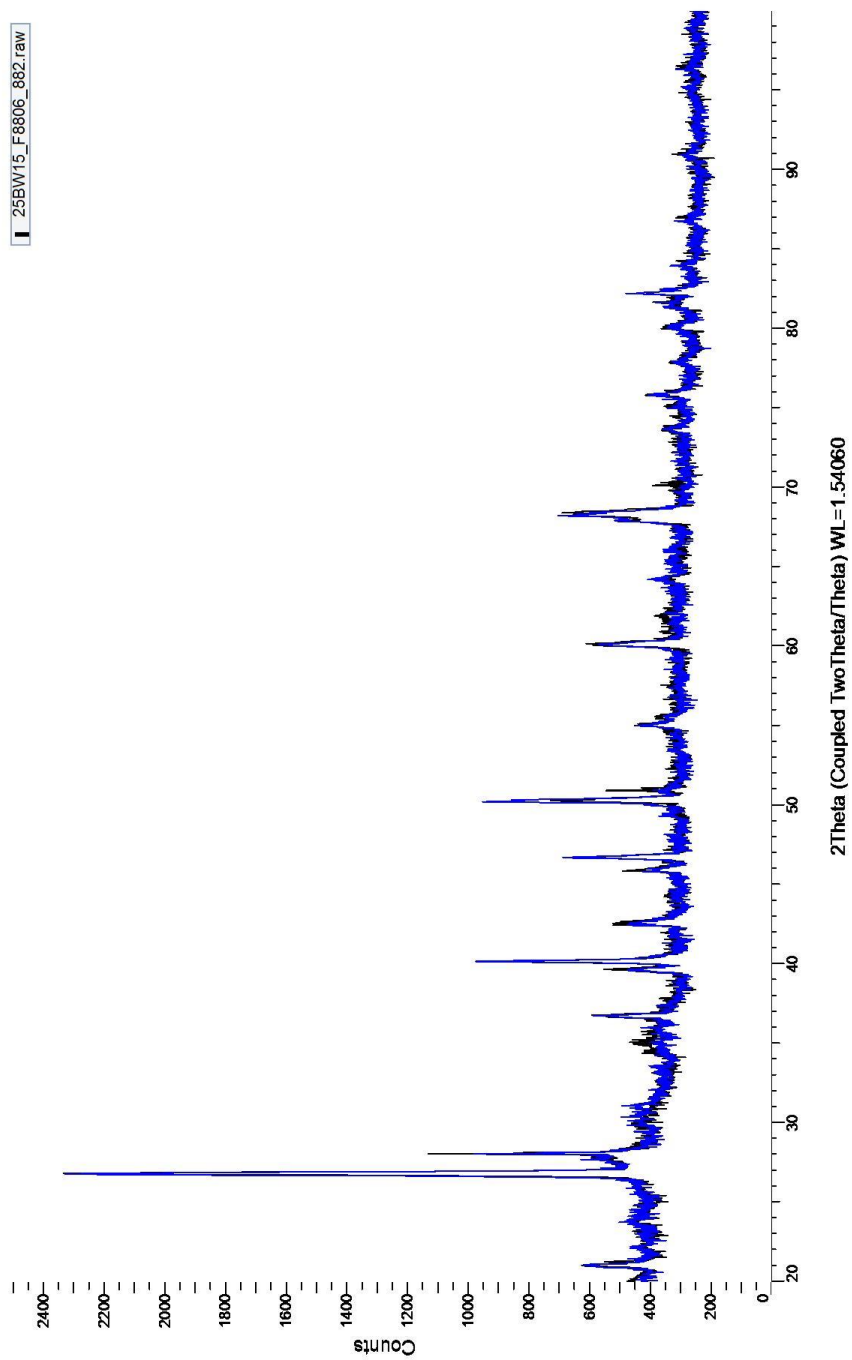
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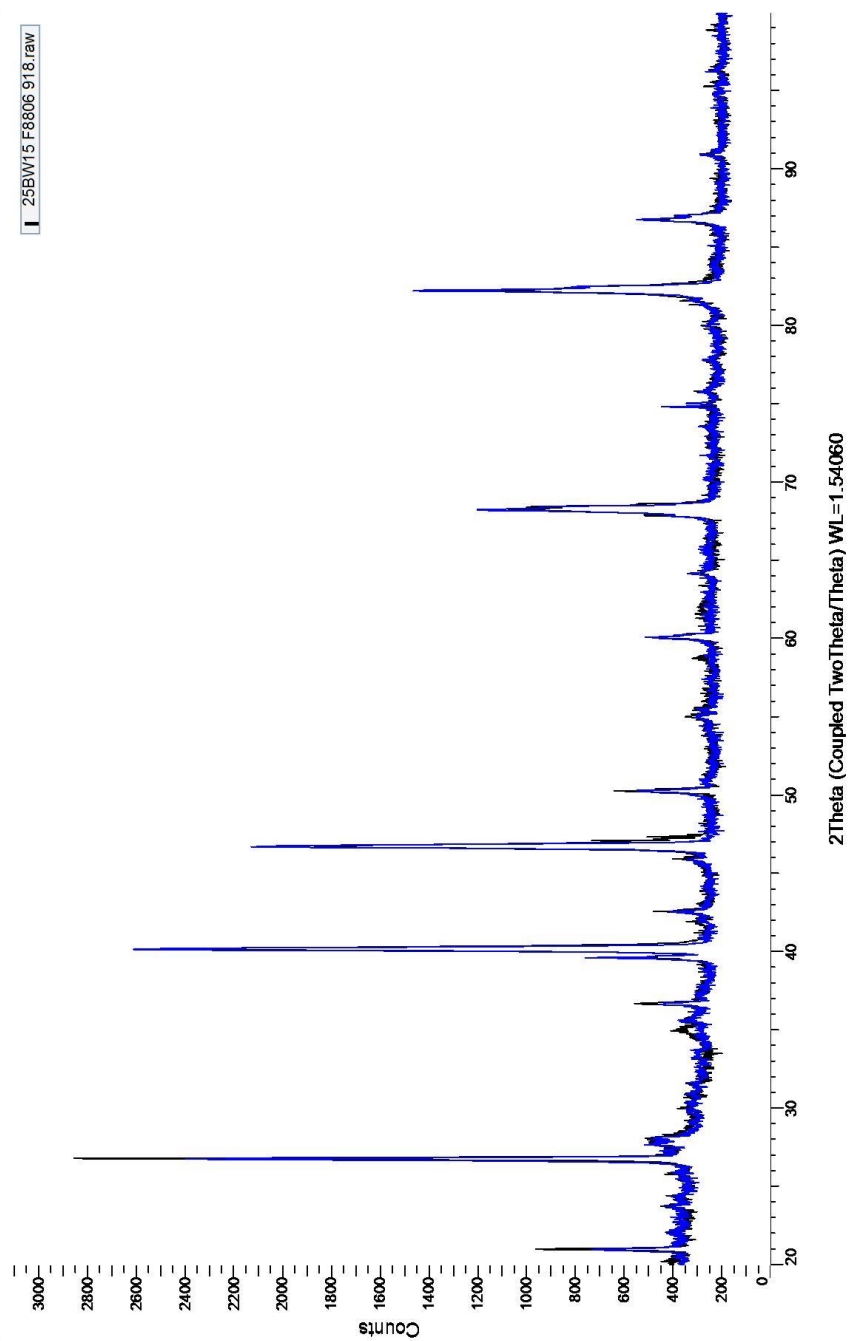
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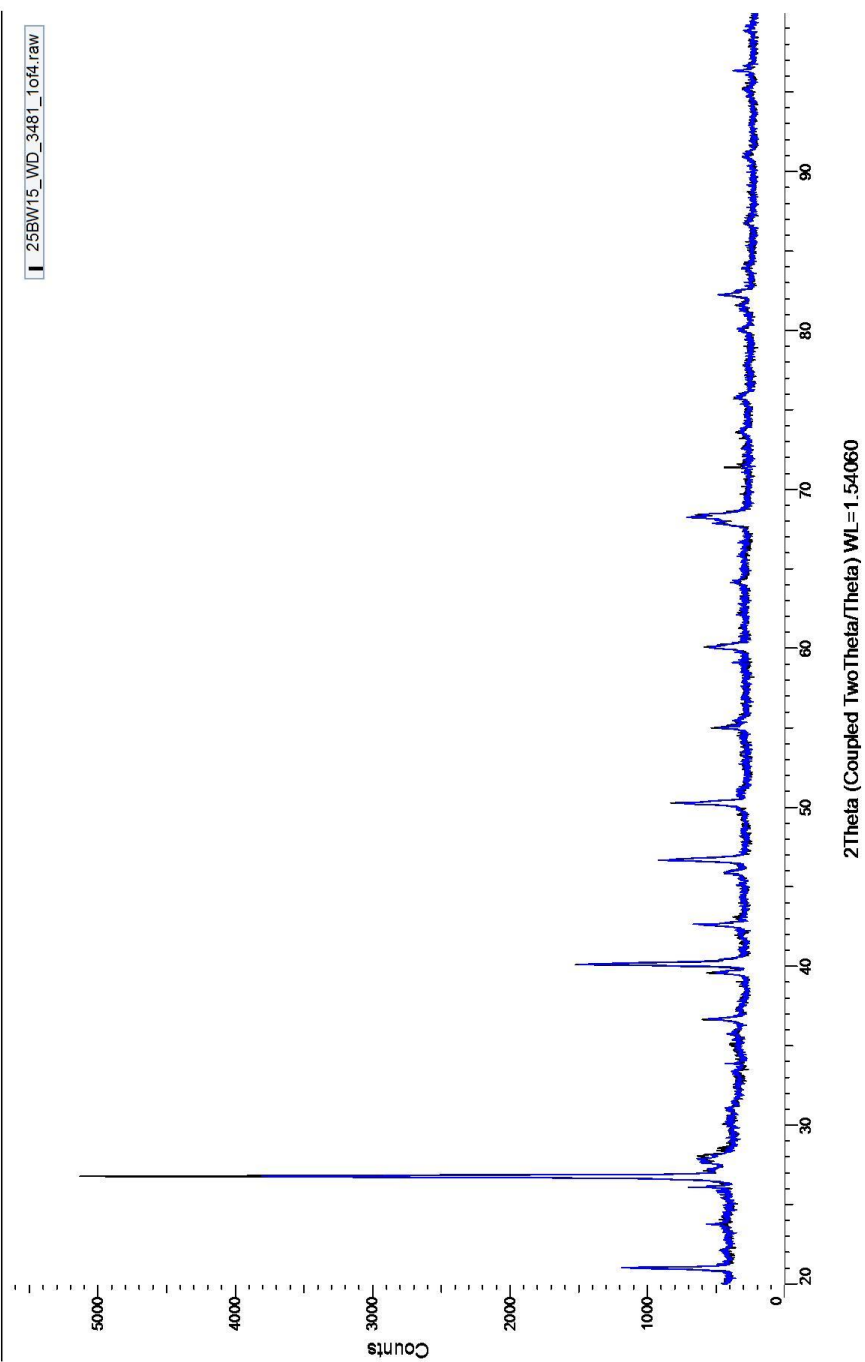
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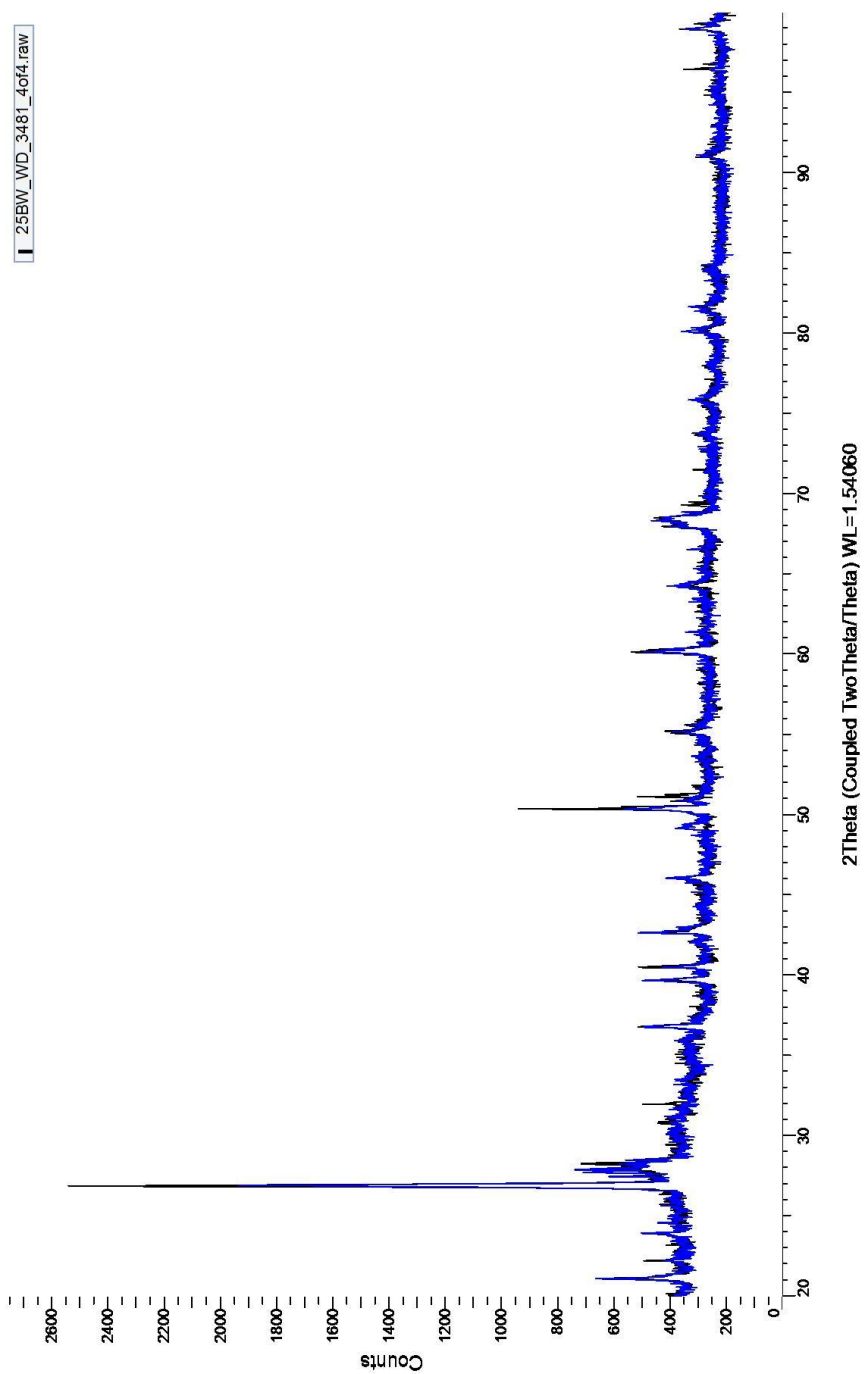
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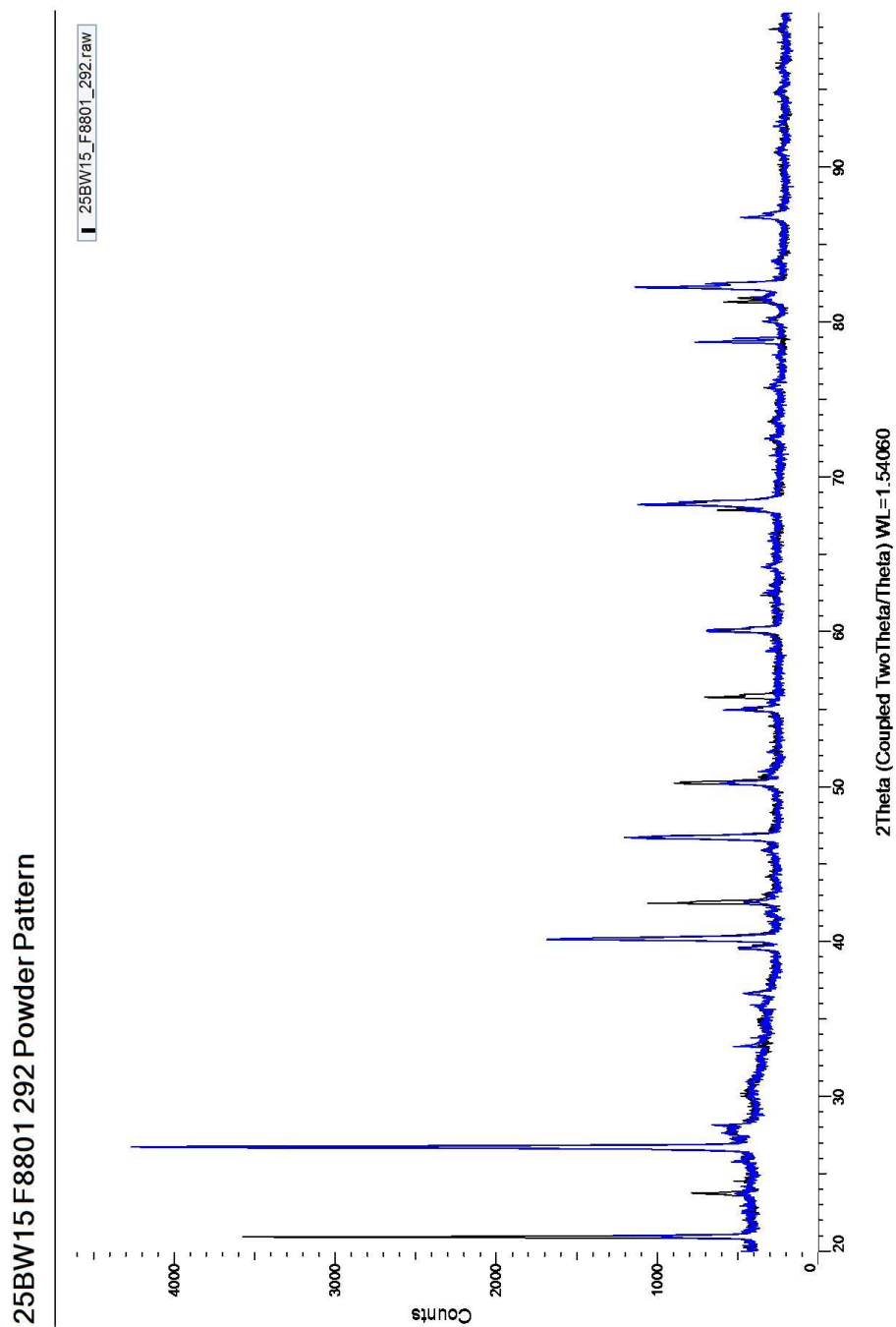
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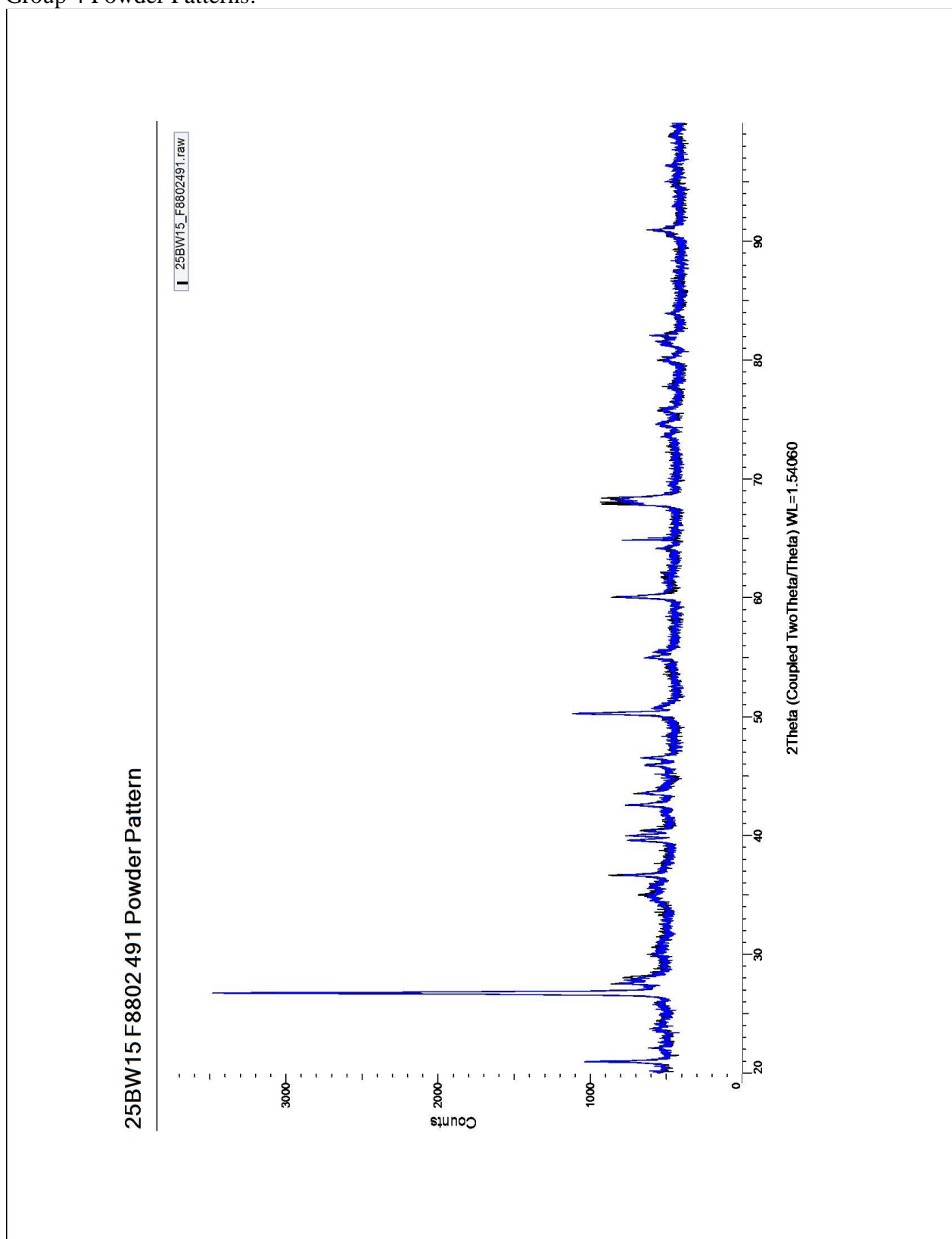
25BW15 Wales Donation 3481 4 of 4 Powder Pattern



Group 3 Powder Patterns:



Group 4 Powder Patterns:



Appendix B: Sample Information Spreadsheet

Sherd ID	Feature #	Site #	Site Name	Sample Photo	XRD Prelim Group	Potential Outlier of Group?	Pigment/Slipped?	Body or Rim
282	F8801	25BW15	McIntosh	Yes	Group 1	No	No	Body
344	F8801	25BW15	McIntosh	Yes	Group 1	No	No	Body
902	F8806	25BW15	McIntosh	Yes	Group 1	No	No	Body
2 of 4	Wales Donation 3481	25BW15	McIntosh	Yes	Group 1	Yes	Pigmentation	Body
3 of 4	Wales Donation 3481	25BW15	McIntosh	No	Group 1	No	Pigmentation	Body
1016	9403	25SY31	Patterson	Yes	Group 1	Yes	No	Body
4017	9411	25SY31	Patterson	Yes	Group 1	Yes	No	Body
8165	9415	25SY31	Patterson	Yes	Group 1	Yes	No	Body
O173	9416	25SY31	Patterson	Yes	Group 1	No	No	Body
131 28	F8701	25BW15	McIntosh	Yes	Group 2	No	No	Body
236 25	F8707	25BW15	McIntosh	Yes	Group 2	No	No	Body
236 29	F8707	25BW15	McIntosh	Yes	Group 2	No	No	Body
236 40	F8707	25BW15	McIntosh	Yes	Group 2	No	No	Body
326	F8801	25BW15	McIntosh	Yes	Group 2	Yes	No	Body
327	F8801	25BW15	McIntosh	Yes	Group 2	No	No	Body
332	F8801	25BW15	McIntosh	Yes	Group 2	No	No	Body
490	F8802	25BW15	McIntosh	Yes	Group 2	Yes	No	Body
872	F8806	25BW15	McIntosh	Yes	Group 2	Yes	No	Body
882	F8806	25BW15	McIntosh	Yes	Group 2	No	No	Body
918	F8806	25BW15	McIntosh	Yes	Group 2	No	No	Body
1 of 4	Wales Donation 3481	25BW15	McIntosh	Yes	Group 2	Yes	Pigmentation	Body
4 of 4	Wales Donation 3481	25BW15	McIntosh	No	Group 2	No	Pigmentation	Body
292	F8801	25BW15	McIntosh	Yes	Group 3	No	No	Body
491	F8802	25BW15	McIntosh	Yes	Group 4	No	No	Body

Sherd ID	Feature #	Site #	Site Name	Characteristic Notes	Comment
282	F8801	25BW15	McIntosh	Square Hole	Sherd sent for NAA (Greiman, 2016)
344	F8801	25BW15	McIntosh		Sherd sent for NAA (Greiman, 2016)
902	F8806	25BW15	McIntosh		
2 of 4	Wales Donation 3481	25BW15	McIntosh	Bright Orange/Red pigment or slip	Photo 3481b, Sherd sent for NAA (Greiman, 2016)
3 of 4	Wales Donation 3481	25BW15	McIntosh	Bright Orange/Red pigment or slip	Sherd sent for NAA (Greiman, 2016)
1016	9403	25SY31	Patterson		
4017	9411	25SY31	Patterson		
8165	9415	25SY31	Patterson		
O173	9416	25SY31	Patterson	Burned; Extremely Hard	
131 28	F8701	25BW15	McIntosh		Sherd sent for NAA (Greiman, 2016)
236 25	F8707	25BW15	McIntosh		Sherd sent for NAA (Greiman, 2016)
236 29	F8707	25BW15	McIntosh	Possibly Burnt Outer Face	Sherd sent for NAA (Greiman, 2016)
236 40	F8707	25BW15	McIntosh		
326	F8801	25BW15	McIntosh	Possibly Burnt Outer Face	Sherd sent for NAA (Greiman, 2016)
327	F8801	25BW15	McIntosh		Sherd sent for NAA (Greiman, 2016)
332	F8801	25BW15	McIntosh		Sherd sent for NAA (Greiman, 2016)
490	F8802	25BW15	McIntosh	Possibly Burnt Outer Face	
872	F8806	25BW15	McIntosh	Burnt Outer Face	
882	F8806	25BW15	McIntosh		Sherd sent for NAA (Greiman, 2016)
918	F8806	25BW15	McIntosh		Sherd sent for NAA (Greiman, 2016)
1 of 4	Wales Donation 3481	25BW15	McIntosh	Bright Orange/Red pigment or slip	Photo 3481a, Sherd sent for NAA (Greiman, 2016)
4 of 4	Wales Donation 3481	25BW15	McIntosh	Bright Orange/Red pigment or slip	Sherd sent for NAA (Greiman, 2016)
292	F8801	25BW15	McIntosh		Sherd sent for NAA (Greiman, 2016)
491	F8802	25BW15	McIntosh		

Appendix C: Sample Photos

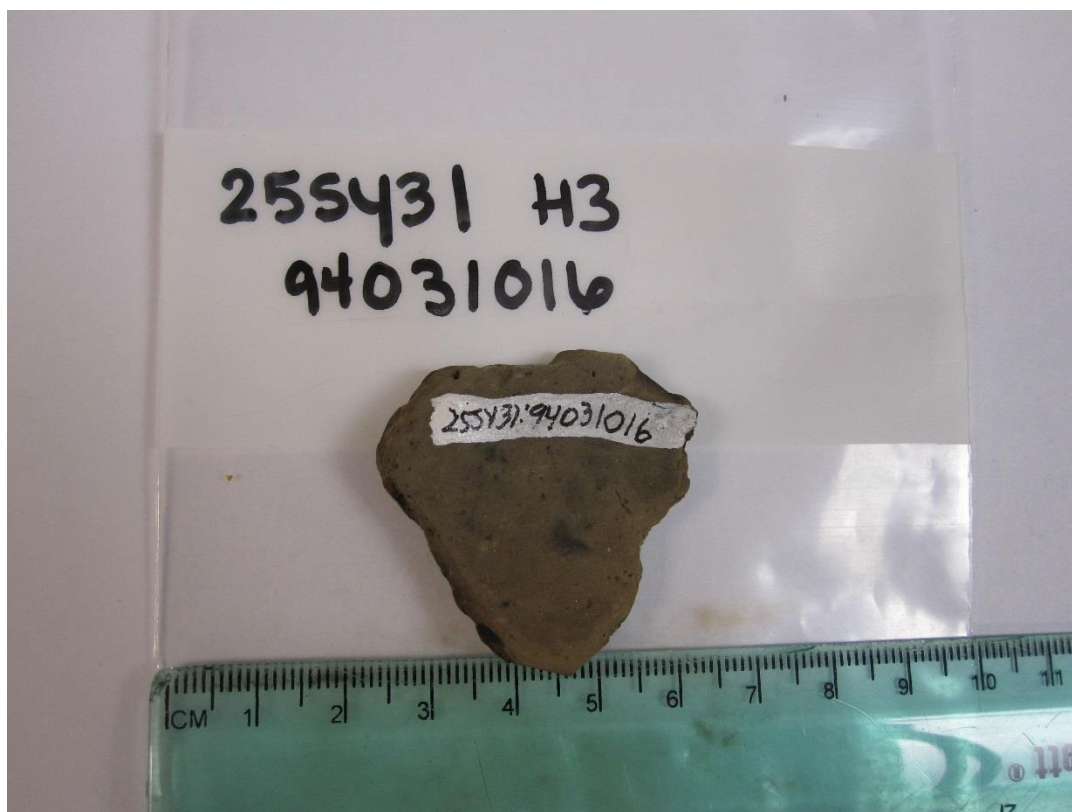
Group 1 Sample Photos:



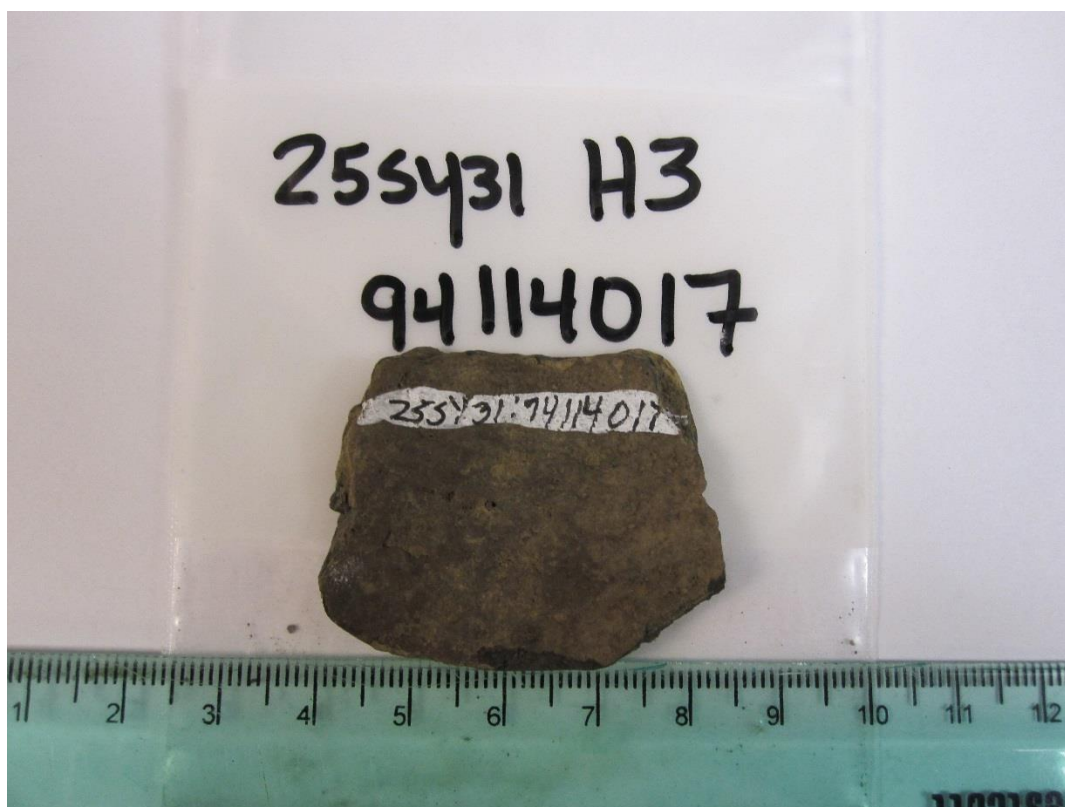
25BW15 F8801 282 Side A and B



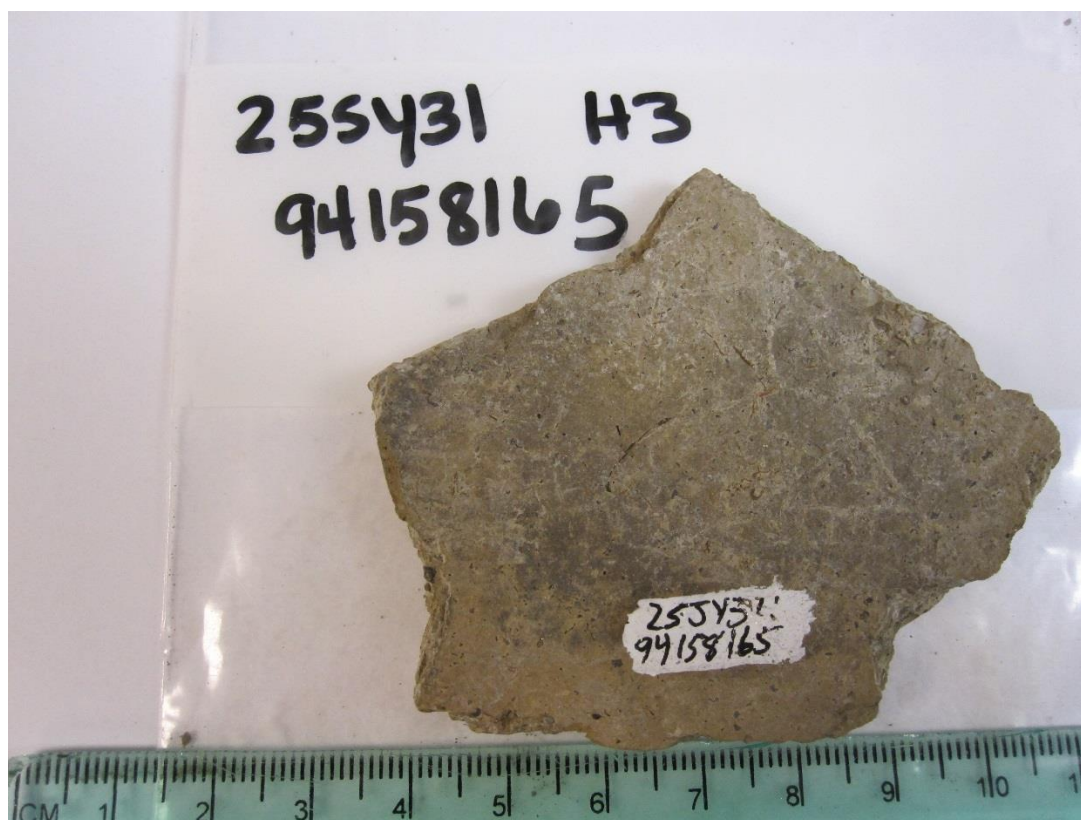
25BW15 F8801 344 Side A and B



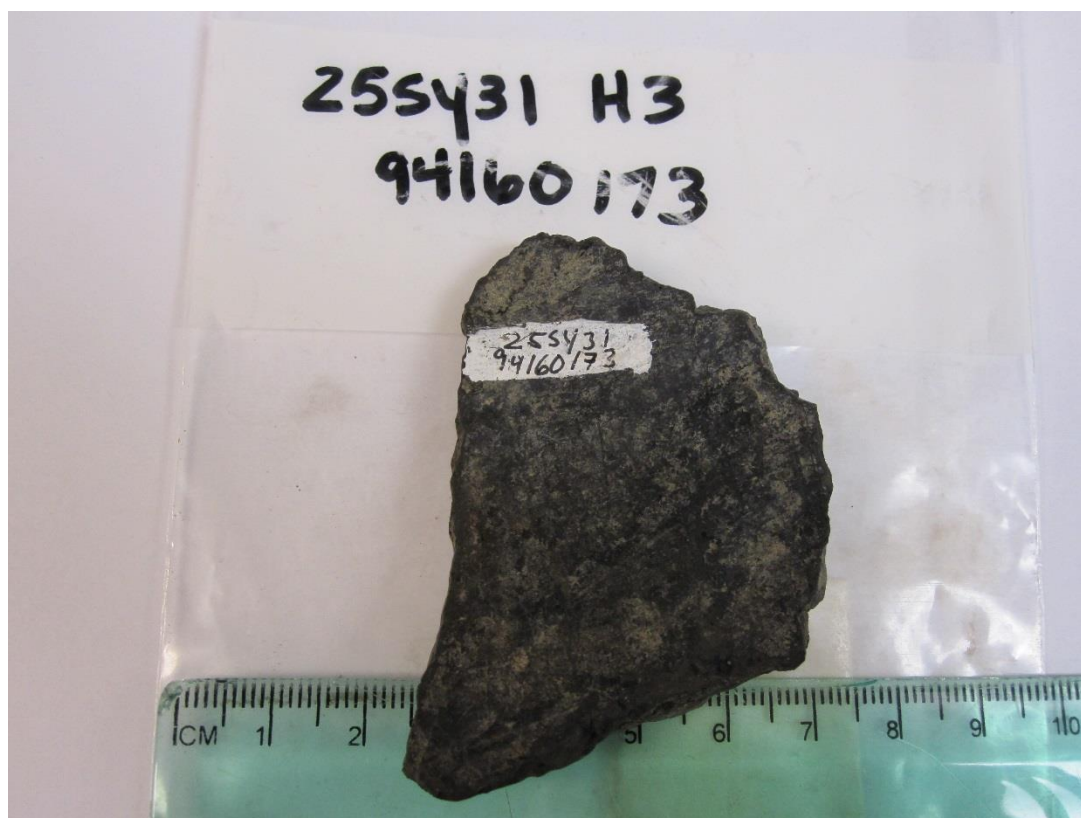
25SY21 H3 94031016 Side A and B



25SY31 H3 94114917 Side A and B



25SY31 H3 94158165 Side A and B



25SY31 H3 94160173 Side A and B

Group 2 Sample Photos:



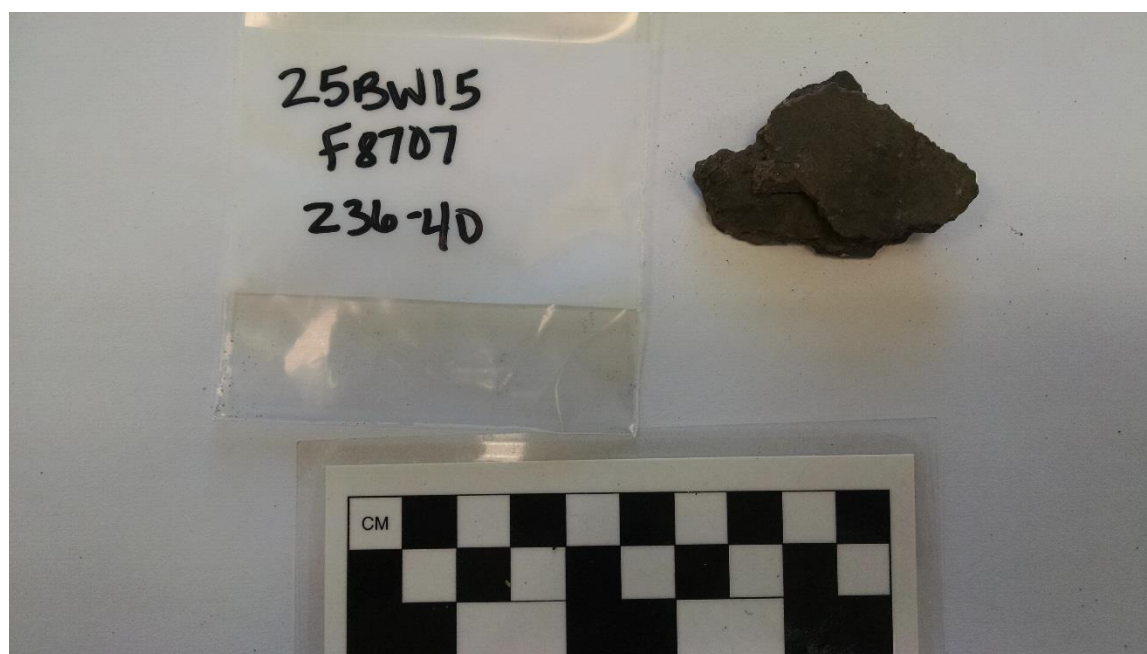
25BW15 F8701 131 28 Side A and B



25BW15 F8707 236 25 Side A and B



25BW15 F8707 236 29 Side A and B



25BW15 F8707 236-40 Side A and B



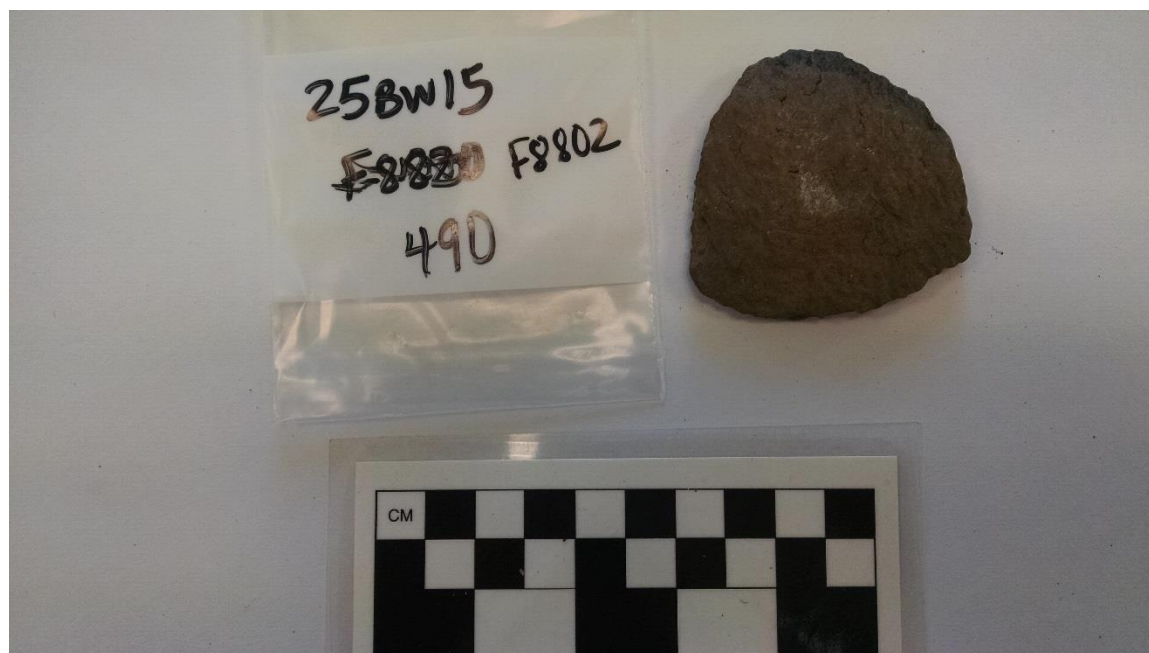
25BW15 F8801 326 Side A and B



25BW15 F8801 327 Side A and B



25BW15 F8801 332 Side A and B



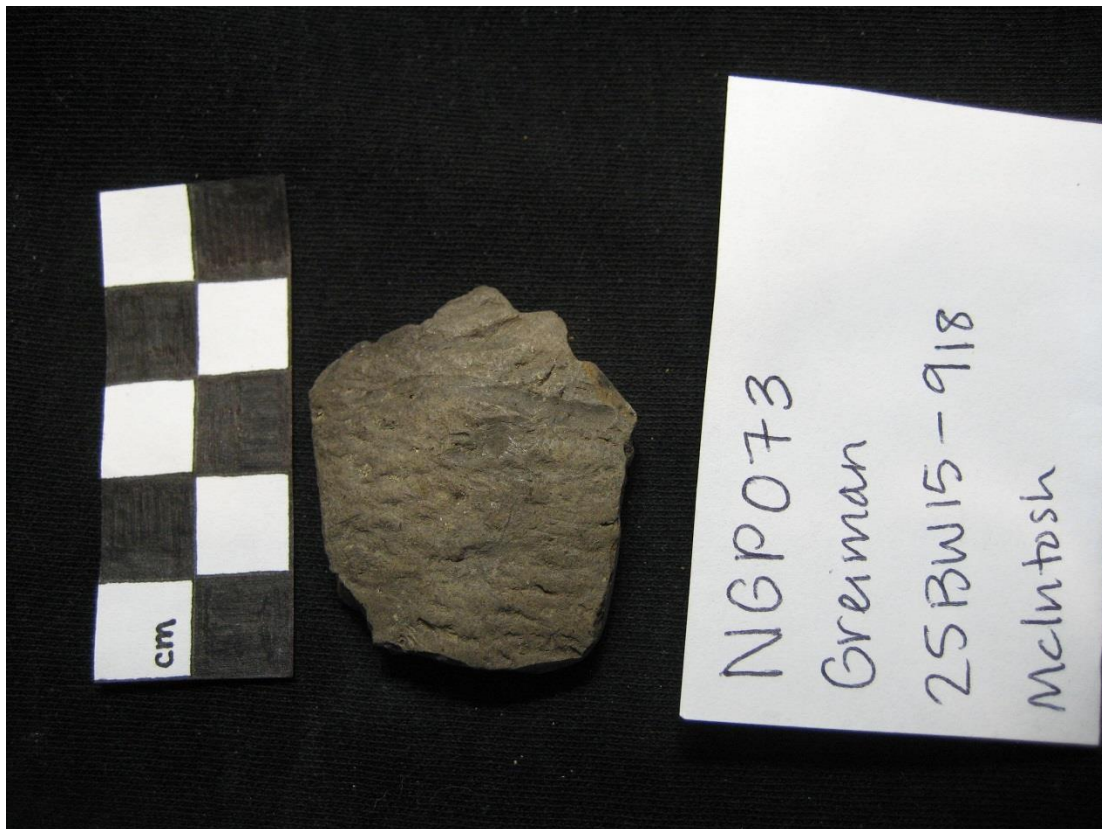
25BW15 F8802 490 Side A and B



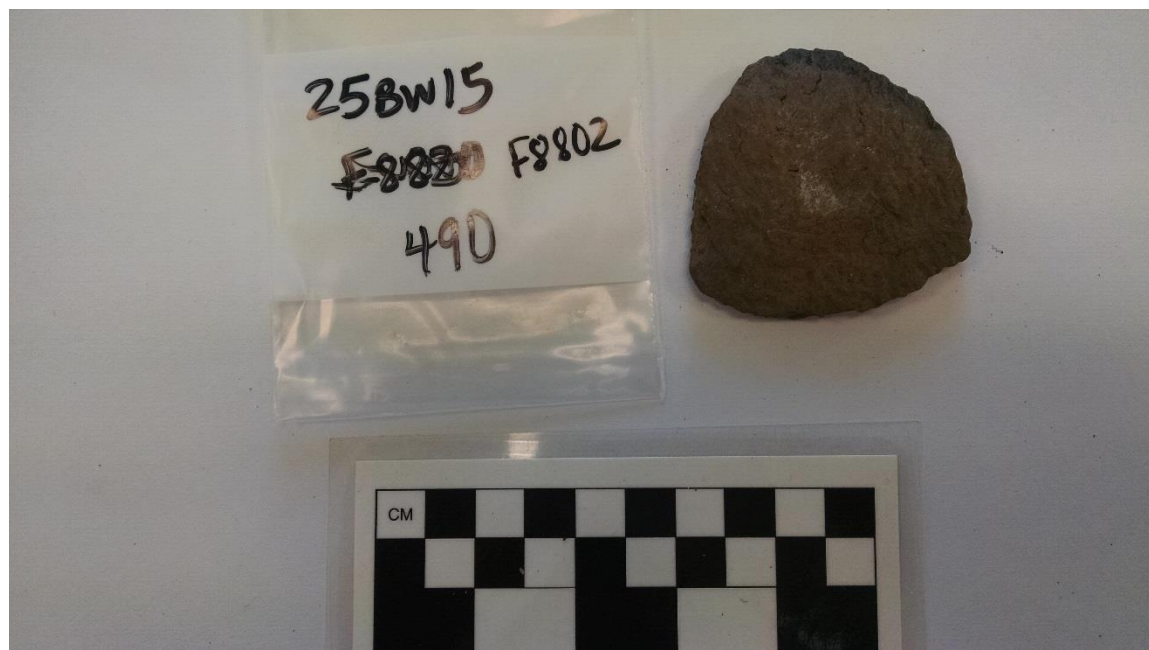
25BW15 F8806 872 Side A and B



25BW15 F8806 882 Side A and B



25BW15 F8806 918 Side A and B



25BW15 F8802 490 side A and B



25BW15 Wales Donation 3481 1 of 4 (3481a) Side A and B

Group 3 Sample Photos:



25BW15 F8801 292 Side A and B

Group 4 Sample Photos:



25BW15 F8802 491 Side A and B