

**Pleistocene Soil Clay Analysis Within Glacial Deposits in Franklin, Pennsylvania**

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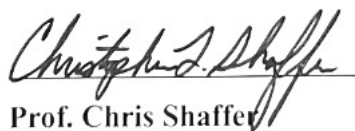
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Submitted in fulfillment of the senior thesis requirements of the  
Department of Geology at Allegheny College  
and approved by the senior thesis committee.

  
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## **Abstract**

Clay grain analysis is used to determine relative soil age through an examination of the isolated grains. Although Optically Stimulated Luminescence (OSL) dating is oftentimes extremely accurate, discrepancies in the data will still be encountered, and using other lab techniques the results can either be validated or voided. In this study, lab instrumentation (XRD, SEM, and EDS) was used to collect quantitative and qualitative data from four soil samples within a glacial deposit and show indicators of possible soil age. Raw data was collected and compared to determine similarities and differences between the soil groupings. The samples showed characteristics of soil development as well as mineralogical maturity, indicating a strong correlation to the older glacial till of Venango County, PA (Mapledale Till) rather than the younger glacial deposits.

## **Acknowledgements**

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## Table of Contents

|       |                                         |     |
|-------|-----------------------------------------|-----|
| I.    | Abstract .....                          | i   |
| II.   | Acknowledgments .....                   | ii  |
| III.  | Table of Contents .....                 | iii |
| IV.   | List of Figures.....                    | iv  |
| V.    | Introduction.....                       | 1   |
|       | A. Glacial Background.....              | 1   |
|       | B. Soil and Clay Dating Techniques..... | 1   |
|       | C. Northwest Pennsylvania.....          | 3   |
| VI.   | Methodology.....                        | 6   |
|       | A. Sample Selection.....                | 6   |
|       | B. Sample Preparation.....              | 6   |
|       | C. Methods of Analysis.....             | 7   |
| VII.  | Results.....                            | 10  |
|       | A. XRD Results .....                    | 10  |
|       | B. SEM and EDS Results.....             | 13  |
| VIII. | Discussion.....                         | 18  |
| IX.   | Conclusion.....                         | 22  |

## List of Figures

|                  |                                                                              |    |
|------------------|------------------------------------------------------------------------------|----|
| Fig. 1:          | Glaciation of Pennsylvania.....                                              | 4  |
| Fig. 2:          | Study Area Map.....                                                          | 6  |
| Fig. 3:          | The Averaged Peak Intensities for Each Sample at 2θ.....                     | 12 |
| Fig. 4:          | XRD Results for Trial 3 of Sample 2 (Btb1) .....                             | 13 |
| Fig. 5:          | Low-Vacuum Scanning Electron Microscopy Image of Sample 2 (Btb1) .....       | 14 |
| Fig. 6:          | High-Vacuum Scanning Electron Microscopy Image of Sample 4 (Btb3) .....      | 14 |
| Fig. 7:          | Low-Vacuum Scanning Electron Microscopy Image of Sample 3 (Btb2) .....       | 15 |
| Fig. 8.1:        | Calculated XRD Patterns of Illite, Smectite, Kaolinite Clay Minerals .....   | 19 |
| Fig. 8.2:        | XRD Study Data with Calculated XRD Pattern Scale.....                        | 19 |
| Fig. 9.1:        | South and West Walls of Vincent Pit.....                                     | 28 |
| Fig. 9.2:        | Detail of the Southeastern Wall of the Vincent Pit.....                      | 28 |
| Fig. 9.3:        | Southeastern Pit Wall of Vincent Pit .....                                   | 29 |
| Fig. 9.4:        | Time-Distance Diagram for Quaternary Glacial Events in NW Pennsylvania ..... | 29 |
| Fig. 10.1:       | Study Samples.....                                                           | 30 |
| Fig. 10.2:       | Rigaku MiniFlex XRD at Allegheny College.....                                | 30 |
| Fig. 10.3:       | Interior of Rigaku MiniFlex XRD.....                                         | 31 |
| Fig. 10.4:       | Rigaku MiniFlex XRD Workstation.....                                         | 31 |
| Fig. 10.5:       | JEOL JSM-6010LV SEM at Allegheny College .....                               | 32 |
| Fig. 10.6:       | Interior of JEOL JSM-6010LV SEM .....                                        | 32 |
| Fig. 11.1-11.4:  | XRD Data Charts of Samples Eb1, Btb1, Btb2, and Btb3.....                    | 33 |
| Fig. 12.1-12.11: | SEM Imagery of Samples Eb1, Btb1, Btb2, and Btb3 .....                       | 37 |

|                                                                  |    |
|------------------------------------------------------------------|----|
| Fig. 13.1-13.4: Spectrum Locations of EDS Data Collection .....  | 43 |
| Table 1: XRD Data Outlining Significant 2 $\theta$ Peaks .....   | 11 |
| Table 2: EDS elemental composition data of sample 1 (Eb1) .....  | 16 |
| Table 3: EDS elemental composition data of sample 2 (Btb1) ..... | 16 |
| Table 4: EDS elemental composition data of sample 3 (Btb2) ..... | 17 |
| Table 5: EDS elemental composition data of sample 4 (Btb3) ..... | 17 |

## **Introduction**

### Glacial Background

Glacial activity is typically associated with sand, gravel and pebble packages. As ice sheets advance and retreat, they erode the landscape and contribute to deposition depending on the existing topography (Braun, 2004). The giant moving ice bodies leave behind mountains, valleys, and deep basins that form geologic systems like the Great Lakes. The glacial deposits known as moraines can span a vast area, outlining the extent of ice sheet advance in the form of fine-grained clays and soils (Crowl and Sevon, 1981). These associated soils are studied to determine accurate dates of glacial coverage between periods of ice sheet advance and retreat which help in furthering the overall understanding of sedimentary geology and climate history (Braun, 2004).

### Soil and Clay Dating Techniques

Soils are categorized into three general age categories based on characteristics that are visible within them such as horizon density and abundance. Young soils typically have very thin horizons and are often lacking whole sections all together. Old soils are the opposite and often consist of thick packages of horizons that differ from each other greatly. Mature soils fall between young and old and typically consist of average thickness horizons with less distinct differences between each. The horizons within old soils also reflect visible differences from one another that are helpful for analysis (Schaetzl and Anderson, 2005).

Soils are formed when the underlying bedrock is constantly stripped and weathered, moving these grains to the location of easiest deposition, commonly valleys (Embleton and King, 1975). There is a direct correlation between the bedrock and soils of an area and the surrounding topography that dictates valleys and other sedimentary structures (Wesley, 2014). Soils are

classified into orders, suborders, great groups, subgroups, and families which are described and organized into state-wide soil surveys (Plowden, 2019). Different characteristics are used to describe these groupings and place them into more specific soil series'. The unique traits that determine the classification of soils are the parent material in which the soil originated from, the overall texture, drainage characteristics, horizon sequence, landscape position, and the overall impact of the surrounding topography (Schaetzl and Anderson, 2005).

Dating soils using different processes can help paint a picture of the geologic history and activity over time within an area. The two most accurate ways in which samples can be lab dated are through Cosmogenic Nuclide Exposure (CNE) dating and Optically Stimulated Luminescence (OSL) dating (Gribenski, 2016). Both techniques, which are very expensive, are used to date surface exposures of glacial moraines that include sand, silt, clays and soils. Other, more accessible analytical techniques are often utilized in the absence of CNE or OSL instrumentation, or when discrepancies are detected in the lab-calculated data. Using visual indicators located within the samples is a commonly practiced method for determining a soil age estimate within an area (Reinhardt, et al., 1988). One of the most significant of these indicators is known as a soil chronosequence which is associated with the nearby horizons. A soil chronosequence is a deposit that shares similar characteristics, yet has differing absolute dates associated with the packages and depicts a chronologically oriented original settling environment (Schaetzl and Anderson, 2005). These sequences are commonly represented by distinct packages with visible indicator clays and other index mineral variations that are exposed to weathering over time, similar to cliffs and other areas of visible erosion and weathering (Retallack, 2001). The chronosequence represented by distinct packages of soils is primarily visible through

indicator clays and elemental similarities that represent similar parent material and origin of deposition.

The mineralogy of clay particles is an important factor for agriculture, engineering, and industrial work (Moore and Reynolds, 1997). In agriculture, the understanding of weathering characteristics and soil clay structure is crucial to ensure efficient farming practices and maximize crop growth. In engineering, the majority of foundational calculations are dependent on the underlying clays that sit beneath structures. In the industrial realm, knowledge of clays is helpful for creating mixtures and compounds like concrete as well as extracting materials from the soils for further processing and use (Moore and Reynolds, 1997). Clay mineralogy not only helps industry, but also provides an avenue of science for further geologic research and the conceptualization of events that have occurred over the course of Earth's history.

#### Northwest Pennsylvania

Northwest Pennsylvania (NWP) was covered by glacial ice sheets during the pre-Illinoian, late-Illinoian, and Wisconsinan Stage of the Pleistocene Epoch during the Quaternary Period (Embleton, 1972). As large bodies of ice advanced inland due to globally decreasing temperatures, the pre-Illinoian Stage (>770,000 yrs.) became the first glaciation event to impact PA, leaving behind unique till deposits that show evidence of the farthest reaching glacial advance period of the Quaternary Ice Age (Figure 1). The late-Illinoian Stage occurred 600,000 years later and was the second farthest reaching glacial advance, happening from 130,000 to 191,000 years ago (Figure 1). The Wisconsinan Stage was the final large glaciation that affected PA, leaving behind several unnamed till deposits that accumulated from 17,000 to 22,000 years ago (Harper and Ward, 1999) (Figure 1).

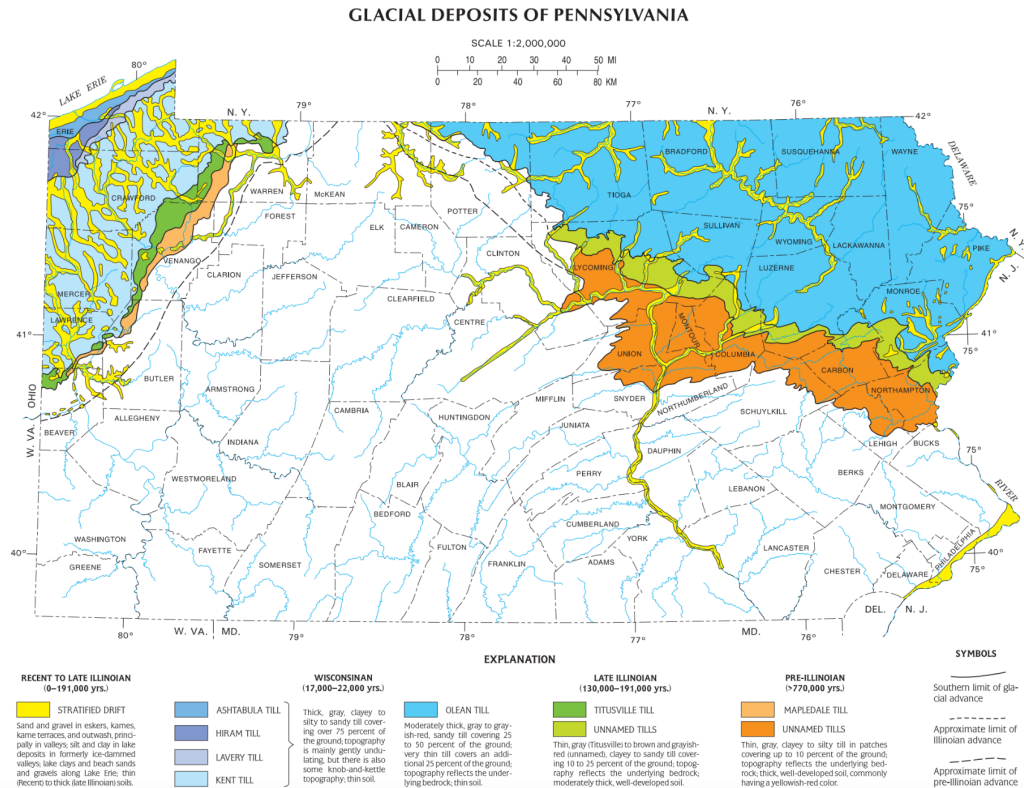


Figure 1. Glaciation of Pennsylvania as well as classification of tills present in deposits and their respective glaciation period (acquired from Sevon, et al., 1999)

During this time, NWPA became covered with allochthonous clasts of igneous and metamorphic rock originating from the Canadian Shield (Sevon, et al., 1999). The low-relief shale basement rock in NWPA was highly resistant to erosion from the overlying Laurentide ice sheet which ensured the primary glacial process to be deposition only, forming the accumulation of sediment known as tills (Braun, 2004). These tills often consist of fine-grained soils with different clay minerals, the most predominant being kaolinite, illite, and smectite (Środoń, 2006). Clay minerals are difficult to distinguish while working in the field due to indistinct grains and packages of isolated clay combined with the soils, but using alternate research methods, individual identifying aspects can be recorded and analyzed within a lab environment (Reinhardt, et al., 1988). Generally, the soils in NWPA originate from coastal environment-deposited parent

material from a time when the land laid host to multiple inland-seas (Blumberg and Cunningham, 1982).

The Vincent Excavating and Gravel pit quarry in Franklin, PA sits on the land boundary of the pre- and late-Illinoian era ice age and represents the far reaches of the glacial expanse in NWPA (Harper and Ward, 1999). The deposits located in the area are the Titusville Till (late Illinoian) and the Mapledale Till (pre-Illinoian). There are also countless unnamed glaciofluvial till deposits in the area, which are categorized as general outwash deposits and are too insignificant to be labeled within a group. The soil geology is represented by two different associations, the Hazleton-Gilpin and the Cookport-Hazleton-Gilpin (Harper and Ward, 1999). These soils are both deep and well-drained, but differ in their process of deposition. The Hazleton-Gilpin association tends to be found along valley walls, whereas the Cookport-Hazleton-Gilpin association occurs primarily in uplands, or high and hilly lands. The underlying rock is primarily from the Mississippian System, which consists of the Shenango Formation (sandstone, shale, and siltstone), Cuyahoga Group (siltstone, shale, and sandstone), Meadville Shale, Sharpsville Sandstone, and the Orangeville Shale (Harper and Ward, 1999).

This analysis is focused on examining pleistocene soils, which are described as thick and abundant packages of soil horizons below the organic zone, or O-horizon (Crowl and Sevon, 1981). Quantitatively and qualitatively understanding soil horizons and the ages of these soils will be beneficial for the interpretation of the overall glacial history and recent ice sheet movement. This study will establish a research baseline of data for clay mineral analysis that can be used as a comparative interpretation tool by future researchers to relatively-date glacial soils.



## Methodology

### Sample Selection

Four samples were taken from within the Vincent Excavating and Gravel Pit in Franklin, Pennsylvania (Figure 2). The samples were collected by Dr. Eric Straffin (PennWest Edinboro University) and provided to Aidan Houlgate for further analysis. The soils were recorded as being from the E-horizon as well as an especially thick package of B-horizon which both sit above the deposited parent rock and basement/bedrock geology in the area. Sample 1 (Eb1) was collected from 0”- 12”, sample 2 (Btb1) was collected from 12”- 24”, sample 3 (Btb2) was collected from 24”- 36”, and sample 4 (Btb3) was collected from 36”- 48” below the excavated topsoil (Figure 10.1).

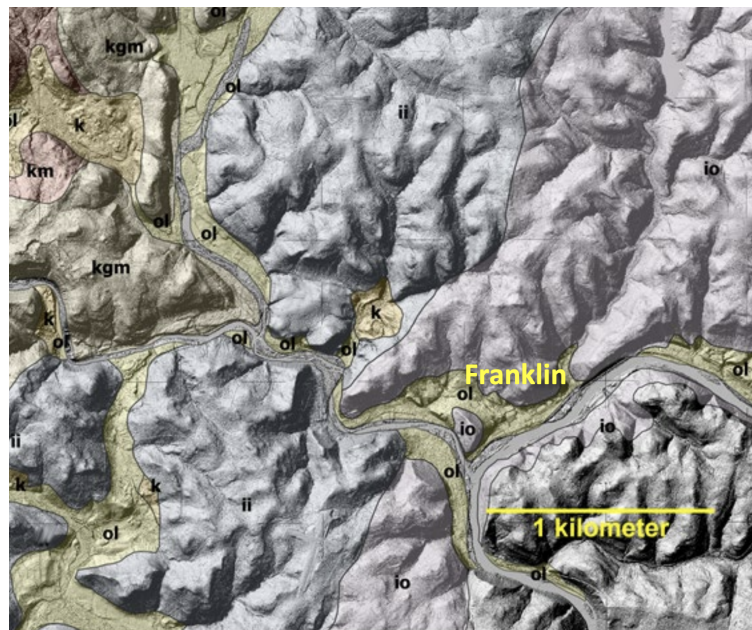


Figure 2. The Vincent and Cooperstown pits are located in the kame deposit (k) in the center of the map. The ‘ii’ is the mapped extent of Titusville Till. ‘io’ is Mapledale Till. ‘km’ and ‘kgm’ are Kent Moraine and ground moraine, respectively. Outwash is labeled ol. Geology from Shepps et al (1959), Plate 1 overlain on 10x lidar hillshade. (Acquired from Fleeger, et al., 2022)

### Sample Preparation

Samples were prepared as oriented aggregate mounts which are used to optimize the data collection within XRD, SEM, and EDS instrumentation (Poppe, et al., 2023). Maintaining the structural integrity of the clay minerals within the samples is crucial to mineralogical analysis. Milling and powdering, which is typically done for XRD analysis, was avoided to retain the mineral crystal structure within the sample (Buhrke, et al., 1998). Instead, suspension-settling was utilized to remove clay minerals from the soil samples. This is done by first using a single-spindle electronic mixer in combination with deionized (DI) water for 20 seconds to form a mixture of soil and clay particles held in suspension within the DI water (Hathaway, 1956). This mixture is then transferred to a beaker and allowed to settle with a resting temperature of 22.2°C, or room temperature (Poppe, et al., 2023). Sodium hexametaphosphate is added to the suspension mixture to act as a dispersant which will help isolate the clay particles from the solution (Poppe, et al., 2023). The beaker is then left for four hours which will allow the non-clay particles to settle at the bottom of the beaker (Poppe, et al., 2023). The particles left in suspension are then primarily clays and the mixture can be removed using a syringe. Using a new beaker with an elevated sample slide placed at the bottom, the extracted mixture is then poured into the receptacle. The new beaker is left at room temperature overnight, or for a period longer than eight hours, which will allow the complete settling of the clay particles onto the elevated sample slide. Once all the water is removed from the beaker, the sample slide is left to air dry for no less than two hours (Poppe, et al., 2023). Once the slide is visibly dry, it is able to be analyzed using lab instrumentation. This preparation process is repeated for the other three samples, ensuring resting temperatures and settling times remain constant.

## Methods of Analysis

Following the sample preparation and once the oriented aggregate mounts are completed, the slides are ready for data collection using the x-ray diffractometer (XRD). X-ray diffraction is a type of data collection that uses a heated x-ray tube held under vacuum conditions to initiate charge to a filament. This filament then emits x-rays which in turn reflect, or bounce, off of the exposed sample tray. The speed at which the x-rays are released from the source tube as well as the time it takes for the control arm holding the tube to move from  $0^{\circ}$  to  $90^{\circ}$  represents the success of the data collection (Figure 9.3) (Flohr, 1997). The standard speed calibration formulated by Princeton University is an accurate method for collecting precise data for several trials of multiple samples within a reasonable time frame. This calibration is known as the Princeton Fast Run (Princeton, 2020). The XRD that is used in this study is the Rigaku MiniFlex Tabletop XRD which is a compact and cost effective x-ray diffractometer (Figure 9.2, 9.3, 9.4) (NanoLab). The XRD is directly connected to a computer system that visualizes live data corresponding to the angle of diffraction from the x-ray filament in relation to the sample. The analytical software associated with the Rigaku MiniFlex are the Rigaku Standard Measurement: Measurement Monitor application (for data collection) and MDI Jade 6.1 application (for data analysis) (Princeton, 2020). Prior to running the sample slides, the XRD was calibrated using USGS Clay Mineral Standard: Kaolinite #5: Larmar Pit, Bath, South Carolina. Other USGS Standards may be used for calibration depending on what is being analyzed. After the machine was calibrated, the samples were ready for data collection. In the case of the Rigaku MiniFlex Tabletop XRD, the sample slides were oriented perpendicular with the diffractometer to obtain consistent results. To ensure precision with the data, each slide was individually tested three times in succession. Following initial data collection with each sample, ethylene glycol was

utilized to expand the clays (Poppe, et al., 2023). This method will only impact the data collection if there is an abundance of swelling and shrinking clays present in the sample, such as smectites (BGS, 2021). To prepare the samples for ethylene glycol treatment, the slides were put into a glass desiccator upon a desiccator shelf. A centimeter depth of ethylene glycol was poured into the desiccator to fill the bottom beneath the shelf, before placing the desiccator in an oven at 65°C for at least four hours and up to 24 hours (Poppe, et al., 2023). It is important to note that the glycol-infused samples must be run in the XRD within 80 minutes after removing the desiccator from the heated oven in order to obtain the swelling and shrinking characteristic data of the clays (ODP, 2003). Each sample was run twice to ensure precision, but to also remain within the 80 minute time constraint (ODP, 2003).

Microscopy is often utilized to analyze fine-grained samples like clays in soils. In the case of very small samples, a scanning electron microscope (SEM) can be used to magnify even the finest grains of matter for visual analysis. The SEM uses electrons emitted from a filament to collect the data. Similar to the XRD system, the SEM is connected to a computer that is programmed to collect data sets from the lab instrument (Swapp, 2017). The instrument used in this study was the JEOL JSM-6010LV (Figure 9.1). The SEM was operated at different conditions to best capture the data. The conditions for slide samples were; high vacuum compression (SEI), 3.0kV-20.0kV, WD8mm-WD12mm, and SS30-SS60. For the clay SEM analysis, each slide was placed individually on an aluminum mount and placed within the vacuum chamber (Figure 9.6). For full soil grain structure microscopy the conditions were; low vacuum compression (LSE), 8.0kV, WD11mm, SS60, 55Pa. For the full soil SEM analysis, an aluminum mount with four non-coated pedestals was utilized to obtain comparative

microstructure imagery and mineralogical composition calculations (Bohor and Hughes, 1971). Backscatter electron mode (BSE) was also used in this study to collect qualitative data.

The energy-dispersive (EDS) detector was utilized to obtain elemental composition of not only crystalline minerals but also amorphous minerals (Goodge, 2017). The EDS used in this study was the Oxford Instruments INCAx-act which was paired with the INCA Energy Software program. To collect data with the EDS, the same procedures for SEM sample preparation were followed (Swapp, 2017). The EDS was calibrated using copper tape placed on the aluminum mount. Each sample was assayed in the Data Collection/Acquire Spectrum procedure for 215-220 seconds, ~1,000,000 counts, and 5 frames to maintain accuracy between the trials. Two trials were performed for each sample in different locations of the slide, at high magnification, in an effort to gather a broad range of mineralogical composition throughout the isolated clay grains. For each clay EDS analysis, nine spectrum locations were used to formulate the data set. Additionally, one trial was executed for each total soil sample without the clays isolated for full-sample context.

## **Results**

The methods used for this research project yielded both quantitative and qualitative data sets. The XRD produced quantitative data in the form of XY axis graphs, the SEM produced qualitative data in the form of high resolution imagery, and the EDS produced quantitative data in the form of mineral percent composition charts.

### **XRD Results**

The XRD data collected for each sample showed several consistent peaks at around  $25^{\circ}2\theta$ ,  $27^{\circ}2\theta$ ,  $13^{\circ}2\theta$ , and  $45^{\circ}2\theta$  (along the X-axis). Each trial for every sample had a primary peak at either  $25^{\circ}2\theta$  or  $27^{\circ}2\theta$  (Table 1). They also exhibited a secondary peak at  $25^{\circ}2\theta$  or  $27^{\circ}2\theta$

(Table 1). Sample 2 (Btb1), sample 3 (Btb2), and sample 4 (Btb3) all had a tertiary peak at  $13^{\circ}2\theta$ . Sample 1 did not have a tertiary peak at  $13^{\circ}2\theta$ , but rather a minor tertiary peak at  $29-31^{\circ}2\theta$  within two of the Sample 1 trials. Sample 2 (Btb1), sample 3 (Btb2), and sample 4 (Btb3) all had a quaternary peak at  $46^{\circ}2\theta$ . Every peak degree exhibited minor decimal variation. The ethylene glycol-treated sample data was averaged to achieve an accurate calculation of two individual trials (Figure 2). The ethylene-glycol treatment did not yield any significant differences between trials. Each sample trial was notated by the corresponding number in order from one to three. The samples listed with a “G” in the name were the trials run after ethylene glycol treatment was applied. The lack of data for sample Btb2-G-2 was due to a file corruption on the XRD connected computer system.

| Sample   | Primary Peak ( $2\theta$ ) | Intensity (cps) | Secondary Peak ( $2\theta$ ) | Intensity (cps) | Tertiary Peak ( $2\theta$ ) | Intensity (cps) | Quaternary Peak ( $2\theta$ ) | Intensity (cps) |
|----------|----------------------------|-----------------|------------------------------|-----------------|-----------------------------|-----------------|-------------------------------|-----------------|
| Eb1-1    | 27.477                     | 431             | 25.959                       | 407             | n/a                         | n/a             | n/a                           | n/a             |
| Eb1-2    | 27.563                     | 432             | 24.673                       | 382             | 31.673                      | 391             | n/a                           | n/a             |
| Eb1-3    | 27.529                     | 449             | 30.55                        | 391             | n/a                         | n/a             | n/a                           | n/a             |
| Eb1-G-1  | 27.556                     | 431             | 26.834                       | 399             | n/a                         | n/a             | n/a                           | n/a             |
| Eb1-G-2  | 27.557                     | 473             | 25.756                       | 306             | 29.107                      | 306             | n/a                           | n/a             |
| Btb1-1   | 27.556                     | 766             | 25.839                       | 671             | 13.359                      | 382             | 46.198                        | 365             |
| Btb1-2   | 27.638                     | 739             | 25.878                       | 707             | 13.32                       | 416             | 46.2                          | 366             |
| Btb1-3   | 27.679                     | 739             | 25.838                       | 665             | 13.318                      | 491             | 46.239                        | 416             |
| Btb1-G-1 | 25.796                     | 756             | 27.554                       | 673             | 13.276                      | 399             | 46.12                         | 332             |
| Btb1-G-2 | 25.797                     | 824             | 27.595                       | 715             | 13.359                      | 366             | 46.358                        | 341             |
| Btb2-1   | 25.879                     | 797             | 27.639                       | 705             | 13.359                      | 398             | 46.198                        | 366             |
| Btb2-2   | 25.919                     | 797             | 27.636                       | 699             | 13.381                      | 357             | 46.237                        | 382             |
| Btb2-3   | 27.597                     | 848             | 25.878                       | 747             | 13.36                       | 416             | 46.279                        | 374             |
| Btb2-G-1 | 27.554                     | 780             | 25.838                       | 631             | 13.318                      | 391             | 46.199                        | 424             |
| Btb2-G-2 | -                          | -               | -                            | -               | -                           | -               | -                             | -               |
| Btb3-1   | 25.878                     | 739             | 27.557                       | 698             | 13.318                      | 349             | 46.237                        | 357             |
| Btb3-2   | 25.839                     | 615             | 27.639                       | 615             | 13.317                      | 432             | 46.159                        | 407             |
| Btb3-3   | 25.758                     | 673             | 27.64                        | 598             | 13.319                      | 342             | 46.238                        | 407             |
| Btb3-G-1 | 27.637                     | 749             | 25.835                       | 631             | 13.24                       | 283             | 46.36                         | 407             |
| Btb3-G-2 | 25.837                     | 716             | 27.599                       | 698             | 13.278                      | 374             | 46.276                        | 407             |

Table 1. Raw XRD data showing the primary, secondary, tertiary, and quaternary peaks at  $2\theta$

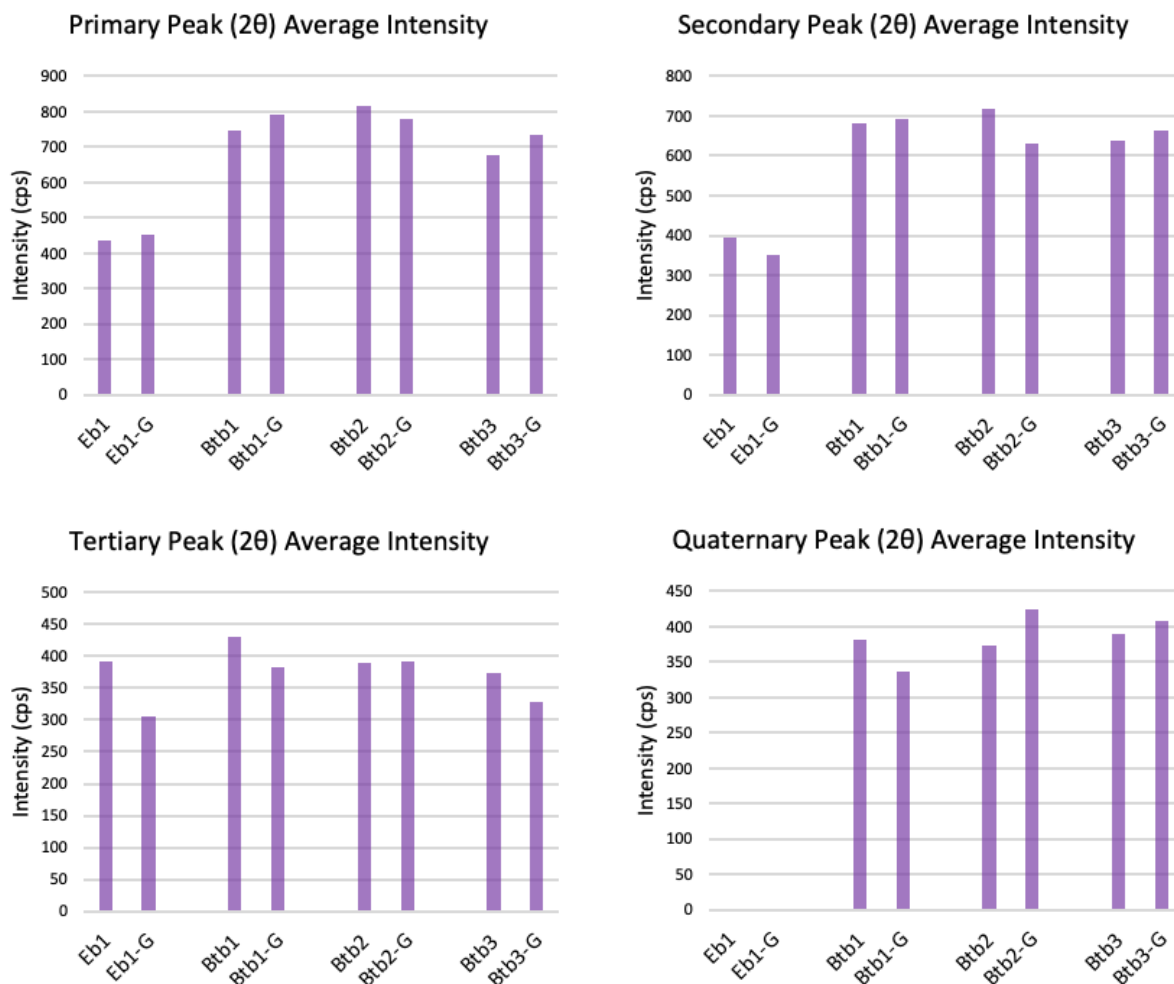


Figure 3. The averaged peak intensities for each sample at each respective peak (2θ). The samples notated with a “G” indicate the ethylene glycol treated trials. The missing data for the quaternary peak of Eb1 and Eb1-G is due to the lack of a significant peak for this sample within the raw data.

Intensity (cps), measured in “counts per second” in relation to the rate of counts per unit time, varied between each sample (Connor, 2019). Figure 3 is an example of the raw XRD results portrayed on an XY axis with respect to the angle of diffraction (2θ) and intensity (cps). The peaks are labeled from the largest significant peak to the smallest significant peak (1: largest, 4: smallest). All XRD results images for sample 1, 2, 3, and 4 are located in the Appendix.

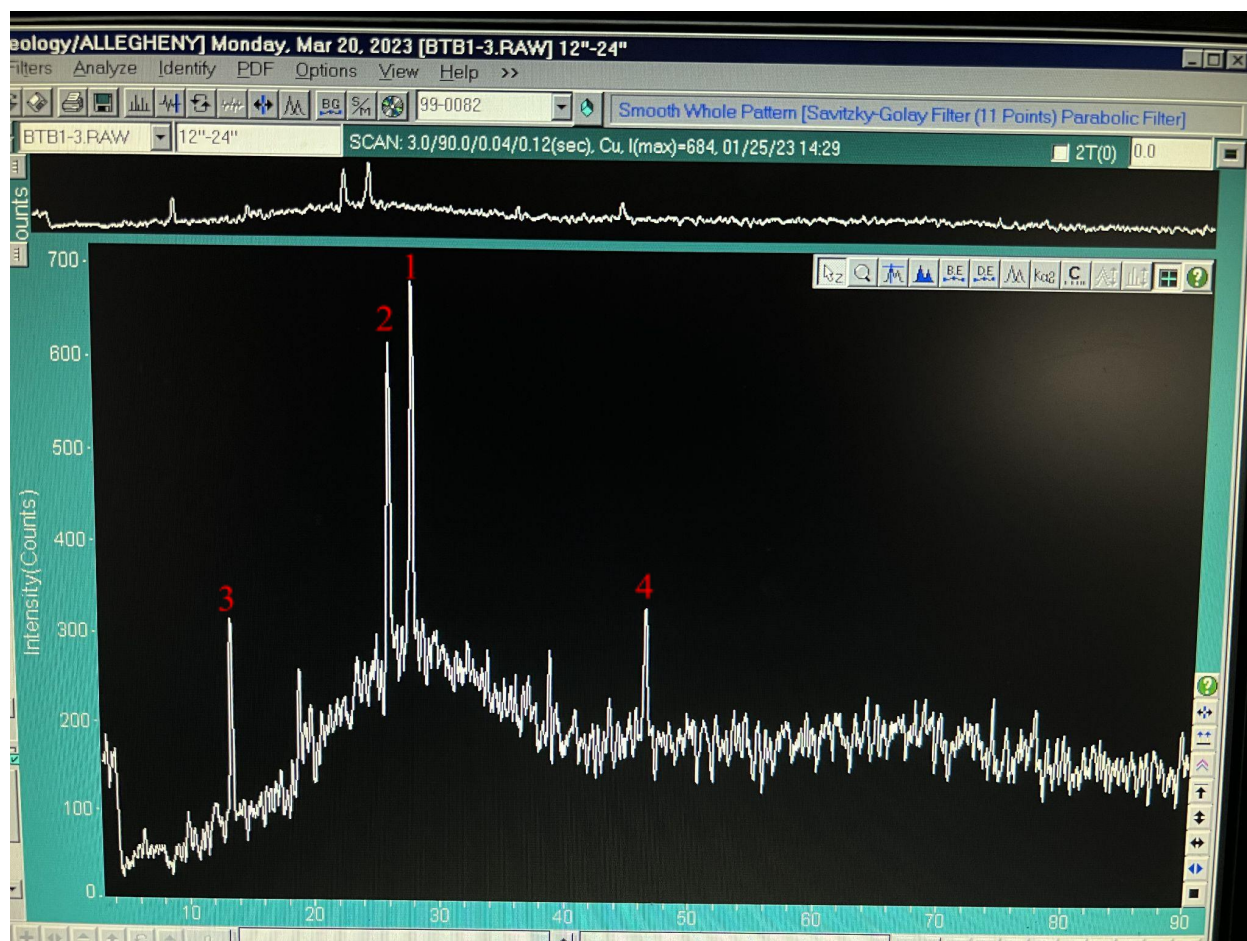


Figure 4. XRD results for sample 2 (Btb1) trial 3, that is portrayed along the X(cps)/Y(2θ) axis showing a primary peak at  $27.679^{\circ}2\theta$  (1), a secondary peak at  $25.838^{\circ}2\theta$  (2), a tertiary peak at  $13.218^{\circ}2\theta$  (3), and a quaternary peak at  $46.239^{\circ}2\theta$  (4) indicated in red numbering. (All other images can be found in the Appendix under *XRD Figures*)

### SEM and EDS Results

The SEM results are depicted in high-resolution imagery at different magnifications and settings. The choice of imagery was dependent on different aspects present within the samples including grain size and shape, grain boundaries, and visible textures and fabrics. The images shown below represent examples of the aspects within the sample thin-sections that were important to this study. Figure 5 is representative of the differing grain sizes and shapes seen in the clays isolated from sample 2 (Btb1). Figure 6 is representative of grain boundaries, grain shape, and the compositional textures seen in the clays isolated from sample 4 (Btb3). Figure 7 is



representative of the overall fabrics and textures within the soil of sample 3 (Btb2) without the clays isolated from the initial sample.

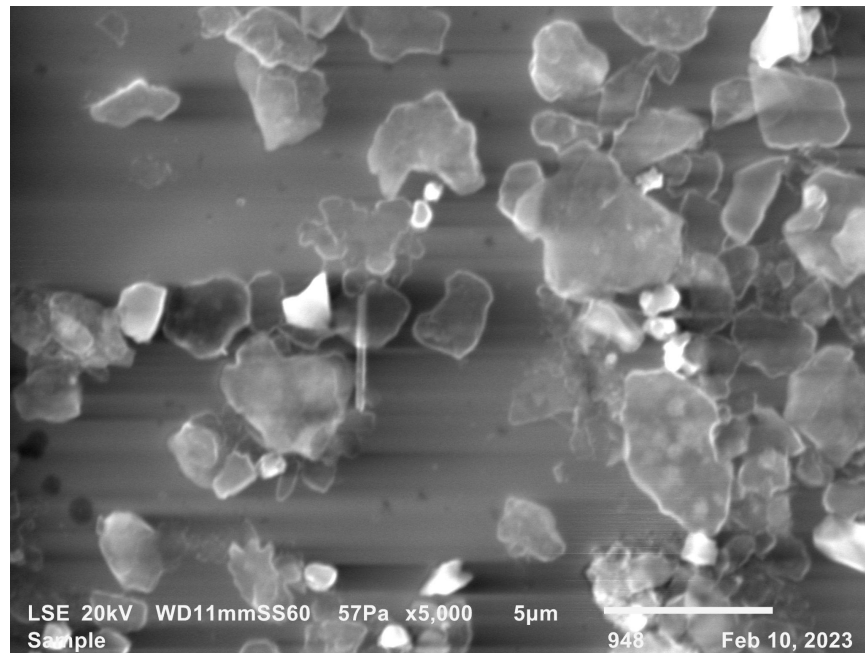


Figure 5. Low-vacuum scanning electron microscopy image of sample 2 (Btb1) showing subangular grain boundaries within isolated clays

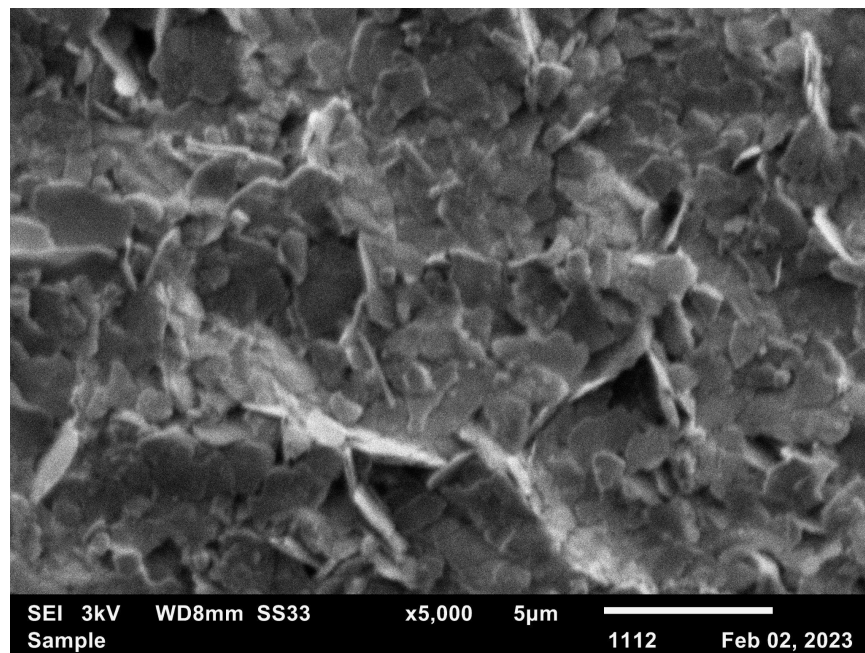


Figure 6. High-vacuum scanning electron microscopy image of sample 4 (Btb3) showing textures and orientations of isolated clay particles

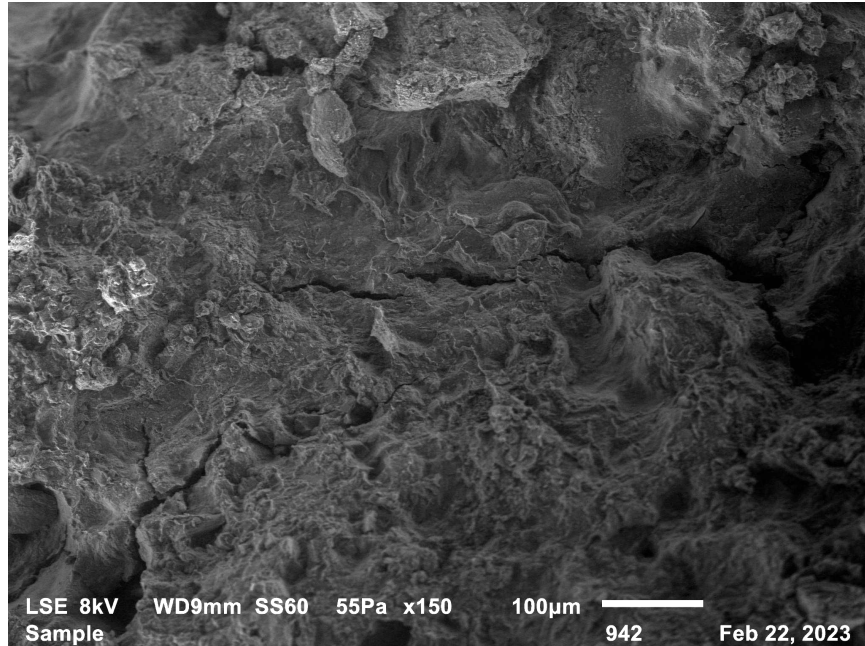


Figure 7. Low-vacuum scanning electron microscopy image of sample 3 (Btb2) showing total soil structures and textures

(All other SEM images can be found in the Appendix under *SEM Figures*)

The EDS results collected from each sample are depicted as quantitative percent composition graphs (Tables 2 - 5) with associated imagery for context (Figures 12.1 - 12.4). The majority of the elemental composition for each sample is *O* (oxygen), and *Si* (silica) with several differences in index minerals such as *Ca* (calcium), *Fe* (iron), and *Al* (aluminum). The highlighted portions of the following four tables indicate the elements that show significant differences between each EDS trial. In sample 1 and 2, the average percent composition of *Ca* is greater than 1.5%, and it drops to below an average of 1.5% in sample 3 and 4. In samples 3 and 4, *Fe* composition is consistently 2% greater than its percent calculation in samples 1 and 2. Samples 3 and 4 also have a consistent increase in *Al* composition by 8-9% from samples 1 and 2.

| <i>Element</i> | <i>O</i> | <i>Na</i> | <i>Mg</i> | <i>Al</i> | <i>Si</i> | <i>S</i> | <i>K</i> | <i>Ca</i> | <i>Fe</i> | <i>Total</i> |
|----------------|----------|-----------|-----------|-----------|-----------|----------|----------|-----------|-----------|--------------|
| Spectrum 1     | 59.11    | 3.19      | 1.25      | 1.87      | 32.43     | 0.11     | 0.26     | 1.56      | 0.23      | 100.00       |
| Spectrum 2     | 59.24    | 3.19      | 1.26      | 1.75      | 32.43     | 0.06     | 0.31     | 1.55      | 0.20      | 100.00       |
| Spectrum 3     | 58.91    | 3.18      | 1.25      | 1.83      | 32.70     | 0.12     | 0.32     | 1.58      | 0.10      | 100.00       |
| Spectrum 4     | 50.57    | 4.33      | 1.90      | 2.07      | 36.96     | 0.11     | 0.43     | 3.46      | 0.17      | 100.00       |
| Spectrum 5     | 48.82    | 4.21      | 1.78      | 2.05      | 38.39     | 0.14     | 0.51     | 3.89      | 0.21      | 100.00       |
| Spectrum 6     | 51.23    | 3.86      | 1.85      | 1.98      | 36.68     | 0.15     | 0.43     | 3.65      | 0.17      | 100.00       |
| Spectrum 7     | 57.13    | 3.27      | 1.41      | 2.65      | 32.91     | 0.10     | 0.48     | 1.82      | 0.22      | 100.00       |
| Spectrum 8     | 54.35    | 3.74      | 1.57      | 2.06      | 35.15     | 0.08     | 0.42     | 2.43      | 0.19      | 100.00       |
| Spectrum 9     | 55.30    | 4.35      | 1.54      | 2.10      | 33.69     | 0.17     | 0.33     | 2.24      | 0.27      | 100.00       |

Table 2. EDS elemental composition data of sample 1 (Eb1) showing total percent composition (%) of the determined elements in the sample, (See Figure 13.1 in *Appendix* for spatial context).

| <i>Element</i> | <i>O</i> | <i>Na</i> | <i>Mg</i> | <i>Al</i> | <i>Si</i> | <i>K</i> | <i>Ca</i> | <i>Ti</i> | <i>Fe</i> | <i>Total</i> |
|----------------|----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|--------------|
| Spectrum 1     | 49.85    | 6.01      | 1.78      | 3.92      | 33.26     | 0.80     | 3.57      | 0.18      | 0.63      | 100.00       |
| Spectrum 2     | 50.39    | 6.08      | 1.71      | 4.00      | 32.71     | 0.92     | 3.50      | 0.11      | 0.58      | 100.00       |
| Spectrum 3     | 49.72    | 6.28      | 1.87      | 3.35      | 33.49     | 0.67     | 3.78      | 0.18      | 0.65      | 100.00       |
| Spectrum 4     | 54.11    | 4.29      | 1.24      | 3.23      | 21.38     | 0.65     | 1.90      | 12.50     | 0.70      | 100.00       |
| Spectrum 5     | 52.85    | 4.12      | 1.18      | 3.20      | 21.86     | 0.63     | 1.99      | 13.52     | 0.65      | 100.00       |
| Spectrum 6     | 52.31    | 4.07      | 1.16      | 3.35      | 22.34     | 0.62     | 1.91      | 13.33     | 0.92      | 100.00       |
| Spectrum 7     | 51.48    | 4.87      | 2.60      | 5.67      | 29.30     | 0.64     | 2.60      | 0.04      | 2.80      | 100.00       |
| Spectrum 8     | 53.55    | 4.62      | 1.39      | 3.62      | 32.50     | 0.64     | 2.71      | 0.20      | 0.78      | 100.00       |
| Spectrum 9     | 52.53    | 4.44      | 1.40      | 3.52      | 34.05     | 0.74     | 2.51      | 0.10      | 0.71      | 100.00       |

Table 3. EDS elemental composition data of sample 2 (Btb1) showing total percent composition (%) of the determined elements in the sample, (See Figure 13.2 in *Appendix* for spatial context).

| <i>Element</i> | <i>O</i> | <i>Na</i> | <i>Mg</i> | <i>Al</i> | <i>Si</i> | <i>P</i> | <i>K</i> | <i>Ca</i> | <i>Ti</i> | <i>Fe</i> | Total  |
|----------------|----------|-----------|-----------|-----------|-----------|----------|----------|-----------|-----------|-----------|--------|
| Spectrum 1     | 54.10    | 1.17      | 0.75      | 11.43     | 24.89     | 0.98     | 2.01     | 0.49      | 0.32      | 3.85      | 100.00 |
| Spectrum 2     | 51.66    | 1.28      | 0.81      | 12.26     | 25.48     | 1.14     | 2.31     | 0.44      | 0.35      | 4.25      | 100.00 |
| Spectrum 3     | 52.56    | 1.10      | 0.82      | 11.89     | 25.88     | 0.97     | 2.16     | 0.55      | 0.44      | 3.63      | 100.00 |
| Spectrum 4     | 52.85    | 0.99      | 0.83      | 11.72     | 24.44     | 0.63     | 2.68     | 0.52      | 1.67      | 3.66      | 100.00 |
| Spectrum 5     | 52.82    | 0.98      | 0.73      | 11.66     | 25.54     | 0.72     | 3.19     | 0.55      | 0.40      | 3.41      | 100.00 |
| Spectrum 6     | 52.92    | 0.92      | 0.86      | 12.37     | 25.14     | 0.65     | 3.11     | 0.57      | 0.42      | 3.05      | 100.00 |
| Spectrum 7     | 52.53    | 1.06      | 0.59      | 10.23     | 28.23     | 0.81     | 1.97     | 0.59      | 0.52      | 3.48      | 100.00 |
| Spectrum 8     | 52.22    | 1.18      | 0.69      | 11.22     | 26.68     | 0.99     | 2.38     | 0.63      | 0.45      | 3.55      | 100.00 |
| Spectrum 9     | 52.37    | 1.07      | 0.93      | 11.89     | 25.14     | 1.03     | 2.39     | 0.81      | 0.69      | 3.69      | 100.00 |

Table 4. EDS elemental composition data of sample 3 (Btb2) showing total percent composition (%) of the determined elements in the sample, (See Figure 13.3 in *Appendix* for spatial context).

| <i>Element</i> | <i>O</i> | <i>Na</i> | <i>Mg</i> | <i>Al</i> | <i>Si</i> | <i>P</i> | <i>K</i> | <i>Ca</i> | <i>Ti</i> | <i>Fe</i> | Total  |
|----------------|----------|-----------|-----------|-----------|-----------|----------|----------|-----------|-----------|-----------|--------|
| Spectrum 1     | 52.54    | 2.01      | 1.00      | 10.61     | 26.12     | 0.25     | 2.76     | 1.44      | 0.43      | 2.84      | 100.00 |
| Spectrum 2     | 52.67    | 1.98      | 0.94      | 10.00     | 27.61     | 0.32     | 2.00     | 1.29      | 0.54      | 2.66      | 100.00 |
| Spectrum 3     | 51.49    | 2.27      | 0.99      | 10.98     | 27.35     | 0.34     | 1.62     | 1.44      | 0.86      | 2.65      | 100.00 |
| Spectrum 4     | 53.04    | 2.10      | 1.06      | 10.32     | 26.53     | 0.34     | 1.83     | 1.24      | 0.41      | 3.13      | 100.00 |
| Spectrum 5     | 52.92    | 2.26      | 0.93      | 10.71     | 25.10     | 0.51     | 2.28     | 1.48      | 0.31      | 3.50      | 100.00 |
| Spectrum 6     | 50.86    | 2.26      | 1.03      | 10.59     | 27.32     | 0.40     | 2.21     | 1.42      | 0.35      | 3.56      | 100.00 |
| Spectrum 7     | 53.43    | 1.91      | 0.89      | 10.98     | 26.45     | 0.29     | 1.88     | 1.20      | 0.35      | 2.63      | 100.00 |
| Spectrum 8     | 53.48    | 1.90      | 0.93      | 11.43     | 26.44     | 0.33     | 1.72     | 1.24      | 0.25      | 2.28      | 100.00 |
| Spectrum 9     | 53.50    | 1.91      | 0.88      | 11.41     | 25.79     | 0.35     | 2.01     | 1.20      | 0.24      | 2.71      | 100.00 |

Table 5. EDS elemental composition data of sample 4 (Btb3) showing total percent composition (%) of the determined elements in the sample, (See Figure 13.4 in *Appendix* for spatial context).

## Discussion

Each of the sample datasets showed similarities to kaolinite and illite, with very little evidence of smectites present in the isolated clay samples. The XRD data determines the possible clay mineral composition of the samples that were tested with a large margin of error. XRD pattern calculations formulated by Jung Ho Ahn of the Korean Ocean Research and Development Institute provide a sound method sufficient for quantitative clay analysis (Ahn, 1992). According to Ahn's method of pattern calculation, the expected results would show significant intensity reference peaks to fall around  $25^{\circ}2\theta$  to  $27^{\circ}2\theta$  (Figure 8.1). The XRD reference peaks produced in this study align with the expected peak results from Ahn's pattern method which indicates a strong presence of kaolinite and illite clay mineral composition (Figure 8.1). There are also significant intensity reference peaks that appear to fall around  $10^{\circ}2\theta$  to  $14^{\circ}2\theta$ , which can be linked to the tertiary intensity peaks found in this study (Figure 8.2). The expected primary peak responsible for indicating the presence of smectite clay minerals would fall around  $5^{\circ}2\theta$  (Figure 8.1, (b)), however there is no evidence of a significant peak at  $5^{\circ}2\theta$  within any of the sample XRD data. The lesser presence of smectite clays within the isolated clays is also apparent due to the ethylene-glycol treatment not yielding any significant differences between the raw trials and the treated trials (Patarachao, et al., 2019). The intensity measurements listed in Table 1 and Figure 2 represent the extent of crystallinity for the clay grains within the tested samples (Kahle, et al., 2002). The differences in maximum intensities between the samples indicate a slight change in percent composition of the particular clay minerals (illite, kaolinite) within each soil horizon (Hughes, et al., 1994). This is outlined in samples 2 and 3, which have higher primary peak intensities than samples 1 and 4. The changes in peak intensities can be interpreted as differing amounts of each specific clay mineral in the collected samples. The data shows that within the sampled soil package, the middle section

(12"-36") has more stable clay grains than both the top section (0"-12") and the bottom section (36"-48"). Using this information, it can be inferred that the clay mineral composition; a significant presence of illite and kaolinite, remains semi-consistent throughout the B soil horizon from the Mapledale and Titusville Tills in Franklin, PA, and the clay mineral composition of the E soil horizon differs slightly in the abundance of the kaolinite and illite clay minerals (Volpi and Szabo, 1988).

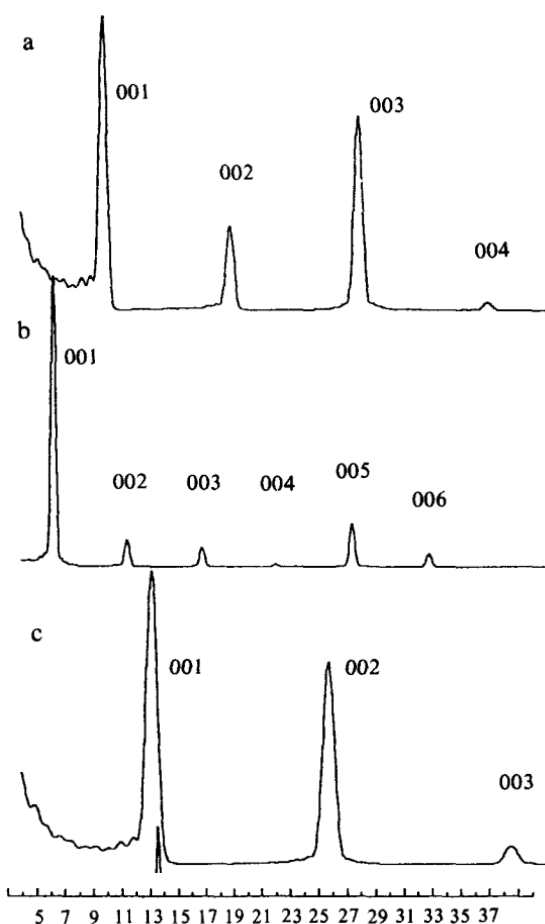


Figure 8.1. Calculated XRD patterns of (a) illite, (b) smectite, (c) kaolinite. (Adapted from Ahn, 1992)

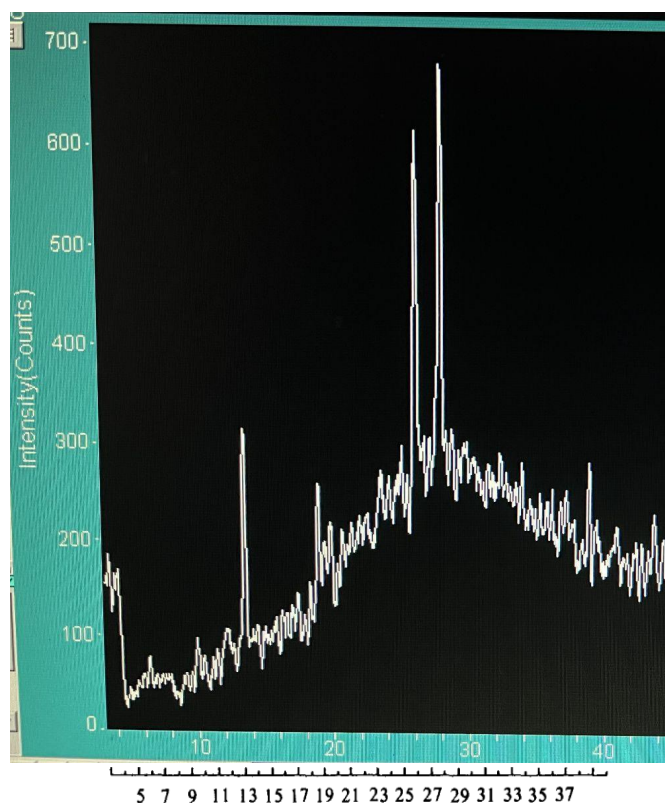


Figure 8.2. Raw XRD data from study with superimposed calculation scale on bottom to allow comparison of data with expected calculations from Ahn.

The collected EDS data in this study agrees with the general clay mineralogical composition data from the XRD statistics. The elements present in the samples remained generally consistent throughout each trial, with several exceptions. The data shows a greater

percent composition of heavier elements (Fe, Al) within samples 3 and 4, which were collected deeper in the soil column (Table 4 and 5). This is likely due to the settling of heavy metals in the older and more established packages of moraine soil. This can also be explained by the breakdown of igneous rocks in an area which contributes to the formation of kaolinite and, in turn, is attributable to the presence of the elements *Al* and *Si* (Schulze, 2005). A greater percent composition of *Ca* is shown in samples 1 and 2 than in samples 3 and 4, signifying that there is more intergranular structure within the clays found in samples 1 and 2 (Table 2 and 3). This is because *Ca* is commonly associated with clay flocculation, or the process of clays aggregating to form larger groupings of connected clays (Dontsova and Norton, 2001). The apparent increase in *K* (potassium) within samples 3 and 4 is worth noting, but it is not a major indicator of any specific clay mineral presence.

The SEM images show several visual indicators of soil age that can assist in the overall analysis. The isolated clays show evidence of maturity and age through the grain roundness (subangular) and the intergranular boundary corrosion and weathering. Additionally, the isolated clays and the total soils both showed evidence of underlying fabrics and structures that indicate pleistocene soils. The significance of grain boundary geometry pertains to the development of soil deposits and the evolution of a related soil chronosequence (Senoussi, et al., 2016). Based on the information about soil age visual indicators (Retallack, 2001) (Reinhardt, et al., 1988), the samples within this study show evidence of early deposition and movement erosion among the clay grains (Figure 12.7 and 12.9). The SEM imagery in this study that focuses on grain geometry shows similar results throughout samples 1, 2, 3, and 4. This is important because it indicates uniformity within the soil horizons. Large differences in grain geometry could be accredited to changes in depositional process, mineralogical differences, or the impact of a

significant geologic event. The differences in grain roundness that are shown in the SEM images of this study indicate textural maturity. Subangular grains depict mature deposits which follow the expected age pattern for typical soil packages (Figure 5, 12.4, and 12.7). In glacial moraines, soils and clays are often deposited in a nonuniform way, creating thorough mixing within soil horizons as well as similarities between the compositions (ie. grain boundaries and grain sizes). The relative-age inferences that can be made from the isolated clays show evidence of accurate alignment towards the development of pleistocene soils and the associated effective weathering processes (Volpi and Szabo, 1988).

There are however aspects of the SEM images that do not follow the interpretations of mature clay composition. These anomalies have been interpreted as different minerals that are fundamentally distinct from the clay minerals. The anomaly hotspots appear brighter in contrast to the clay grains within the matrix due to the SEM filament overcharging electrons on the sample slide within the vacuum chamber. Despite possibly having a negative impact on the samples, this phenomenon is effectively harmless and actually helps to determine which grains are generally alike in composition. This comparison is helpful for analyzing specific data points, as well as avoiding anomalies while using the EDS instrument and its associated computer software.

The textures that were discovered in the isolated clay samples are also significant to the relative-age interpretations of the soils. These structures are made up of interlocking clay grains that form as the isolated clays are accumulated onto the sample slide. Some of the grains are oriented perpendicular and vertical to one another, depicting a flow structure that can be attributed to the cohesion of the illite and kaolinite clay minerals as well as the presence of *Ca* (Figure 11.9 and 11.11). The mentioned structures are not indicators of exact age, but rather



factors of comparison that can be used between samples to determine depositional patterns and similarities. Significant fabric structures and textures were found in all four of the samples likely due to the interlocking of clay grains discussed above. Samples 1 and 2 show more predominant evidence of underlying textures (Figure 11.1) that can be attributed to larger aggregates of grains interlocking due to the greater percent composition of Ca, which in turn causes greater clay flocculation and connective structures (Dontsova and Norton, 2001).

The contextual meaning for the research conducted in this study is to connect the glacial retreat and advance over NWPA of the pre-Illinoian, late-Illinoian, and Wisconsinan Stage of the Pleistocene Epoch during the Quaternary Period of geologic time (Harper and Ward, 1999). As described in the Introduction, the expected glacial deposits in the sample area are the Mapledale Till and the Titusville Till. The soils were deposited before the O horizon, and because the soils exemplify indicators of older deposition and weathering, it can be inferred that the majority of the till composition in the study area relates solely to the Mapledale Till deposit (Volpi and Szabo, 1988). The intermixing of weathered inland-sea soil deposits and allochthonous weathered igneous deposits can explain the clay composition found in the samples from the Vincent Pit in Franklin, PA. The exact age of the ice sheet advance and retreat is still in question, but the relative-age of the soil group at this location was verified through the elemental composition of the included clay minerals as well as the visual indicators of soil development during this study.

## **Conclusion**

Applying the data collected with XRD, SEM, and EDS instrumentation, this study determined visual and mineralogical indicators of the relative-age of the pleistocene soil deposits located at the Vincent Excavating and Gravel pit in Franklin, PA. The datasets from this study

contributed to the overall quantitative and qualitative clay mineral analysis collection of soil data in the scientific community, helping to create a new comparative research baseline for further study and interpretation. The main limiting factor that was encountered during this study was human error during sample preparation and data collection, which includes sample handling and storage. This research project can be replicated using similar methodology on any soil sample with clay mineral content. Increasing sample accuracy by collecting and testing more samples would allow for the procedures outlined in the Methodology to have an increased effectiveness when forming inferences and interpretations. The information determined in this study will be used as a point of comparison between different soil deposits composed of clay and other fine-grained minerals for further scientific research.

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## Appendix

### *Introduction Figures*



Figure 9.1. South (distant) and west (right side) walls of Vincent Pit. (Acquired from Fleegeer, et al., 2022)

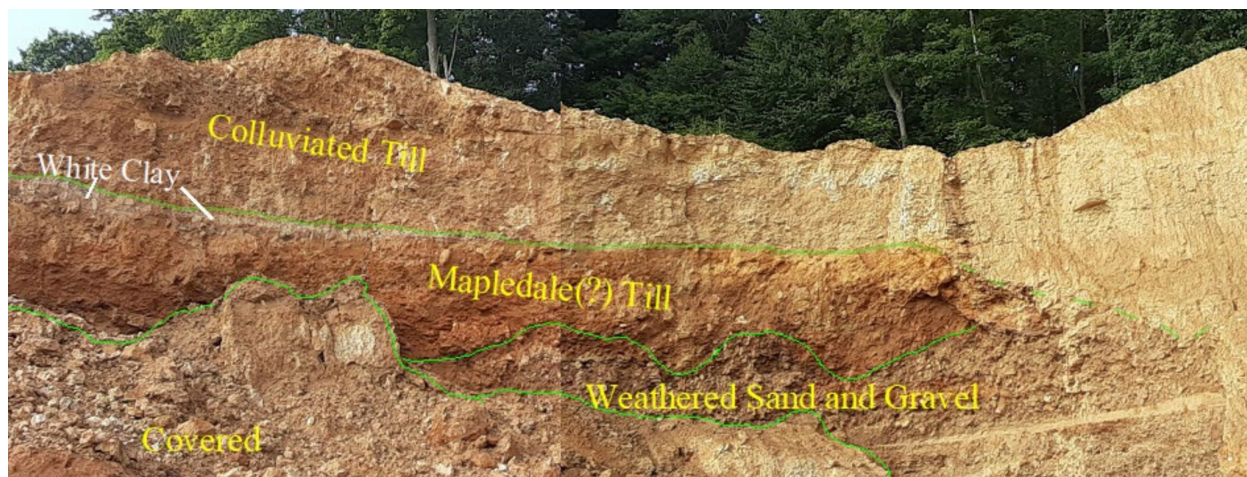


Figure 9.2. Detail of the southeastern wall of the Vincent Pit. (Acquired from Fleegeer, et al., 2022)





Figure 9.3. Southeastern pit wall, Vincent Pit. Cross bedded sand and gravel lenses at base of pit, overlain by dark, cemented sand and gravel, and till. (Acquired from Fleegeer, et al., 2022)

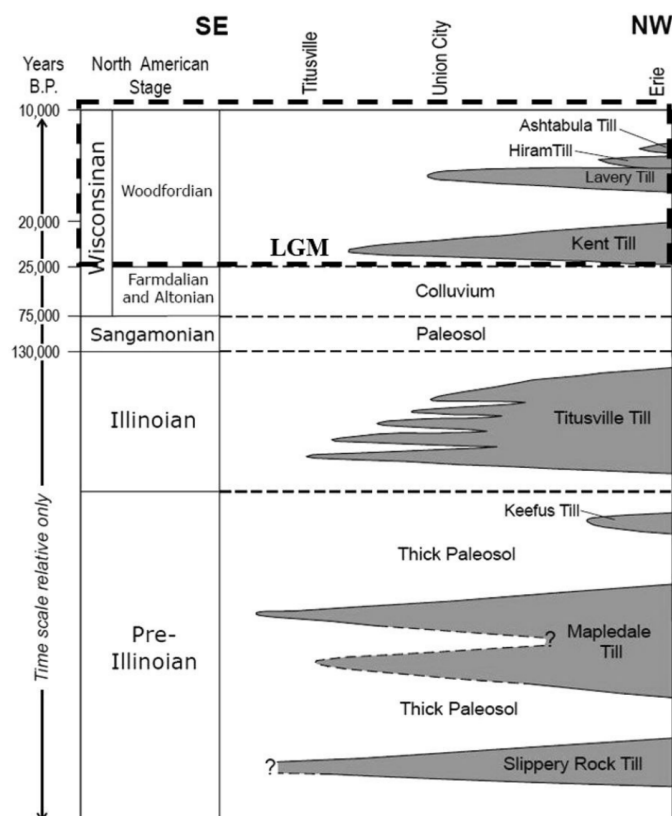


Figure 9.4. Time-distance diagram for Quaternary glacial events in northwestern Pennsylvania. Franklin is located to the left of the Titusville location marker. The Late glacial maximum (LGM) which is represented by the Kent Till (originally from Fleegeer, et al. 2011). (Acquired from Grote and Straffin, 2019)



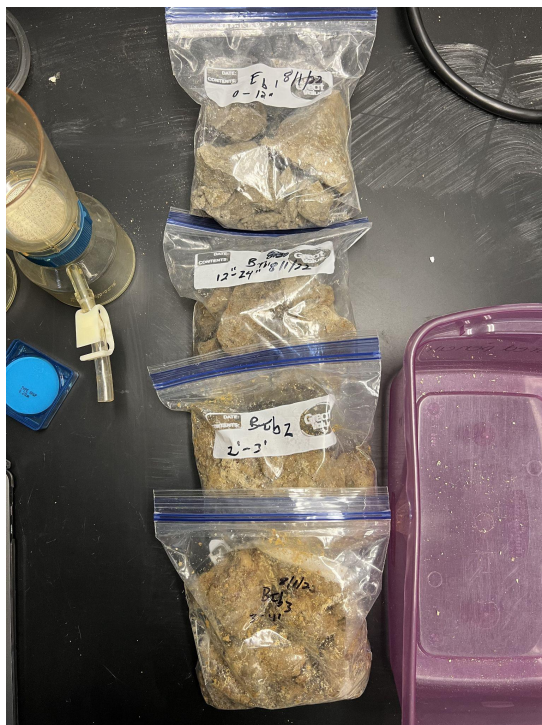
*Methodology Figures*

Figure 10.1. The four samples, in order from the middle of the B Horizon (Btb3) to the bottom of the E horizon (Eb1).



Figure 10.2. Rigaku MiniFlex XRD at Allegheny College.



Figure 10.3. Sample bay and X-ray control arm of Rigaku MiniFlex XRD.



Figure 10.4. Rigaku MiniFlex XRD with attached cooling system (below XRD) and the associated computer with the necessary software for data acquisition and analysis.



Figure 10.5. JEOL JSM-6010LV SEM at Allegheny College.

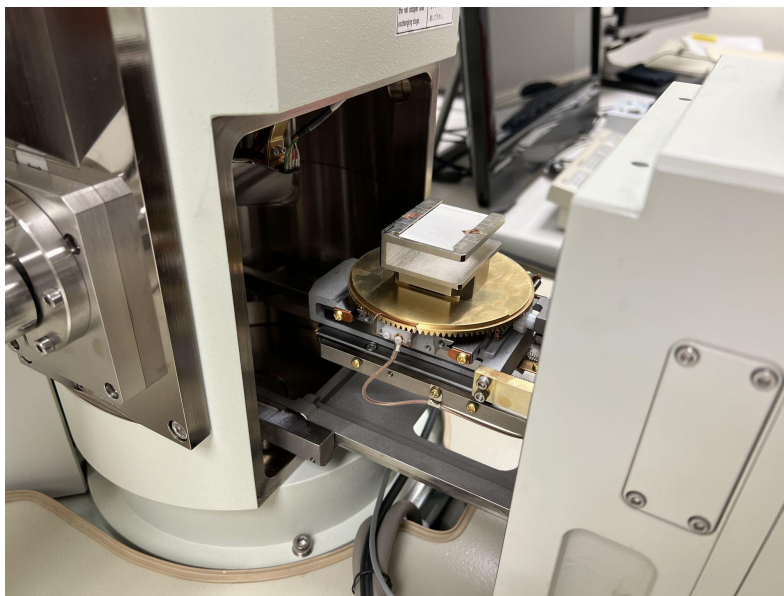


Figure 10.6. JEOL JSM-6010LV SEM sample stage pulled out from the vacuum chamber.



## XRD Figures

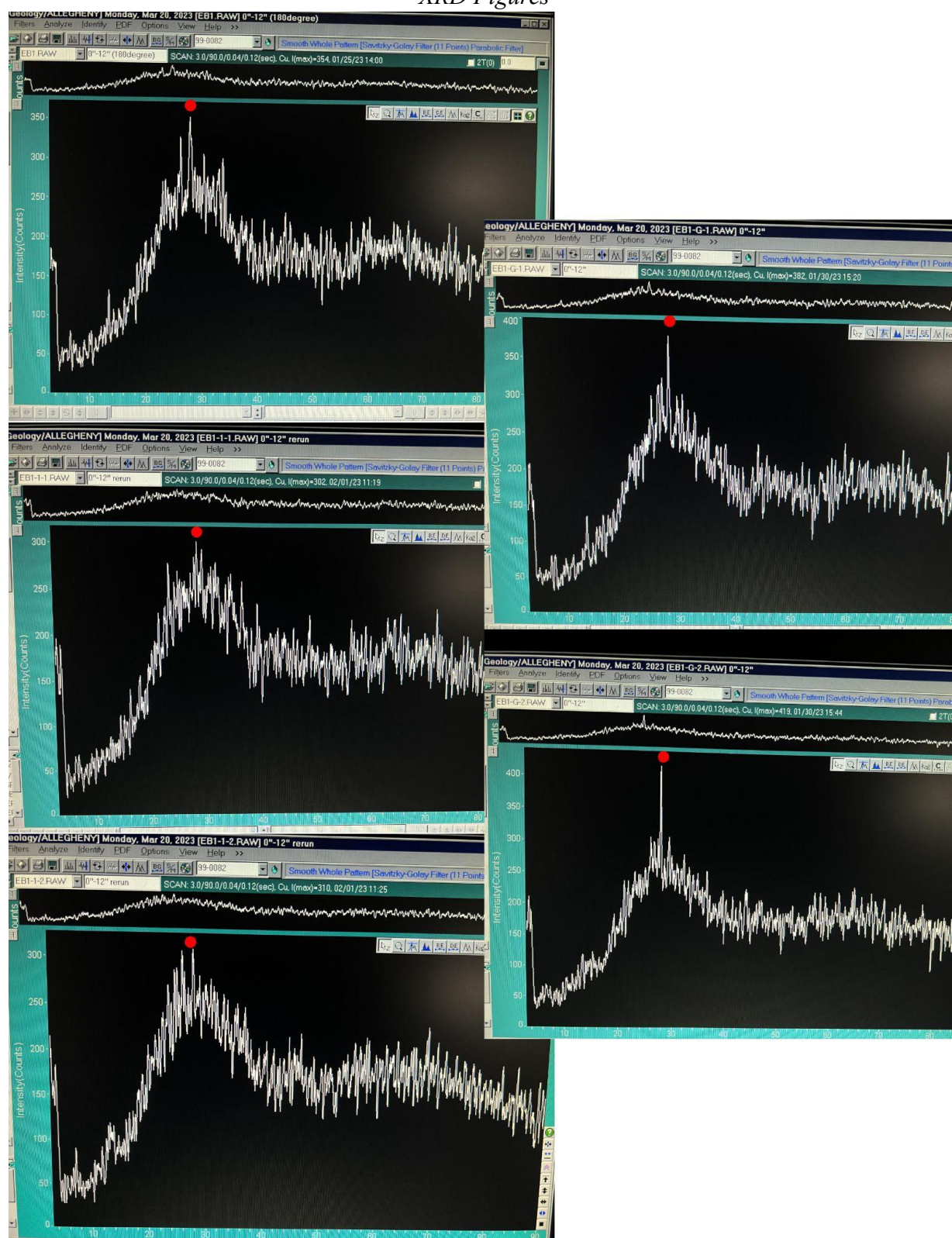


Figure 11.1. Raw XRD data charts of Sample Eb1, red dot indicates primary peak (raw trials 1, 2, 3 from top down on left, ethylene glycol treated trials 1, 2 from top down on right).

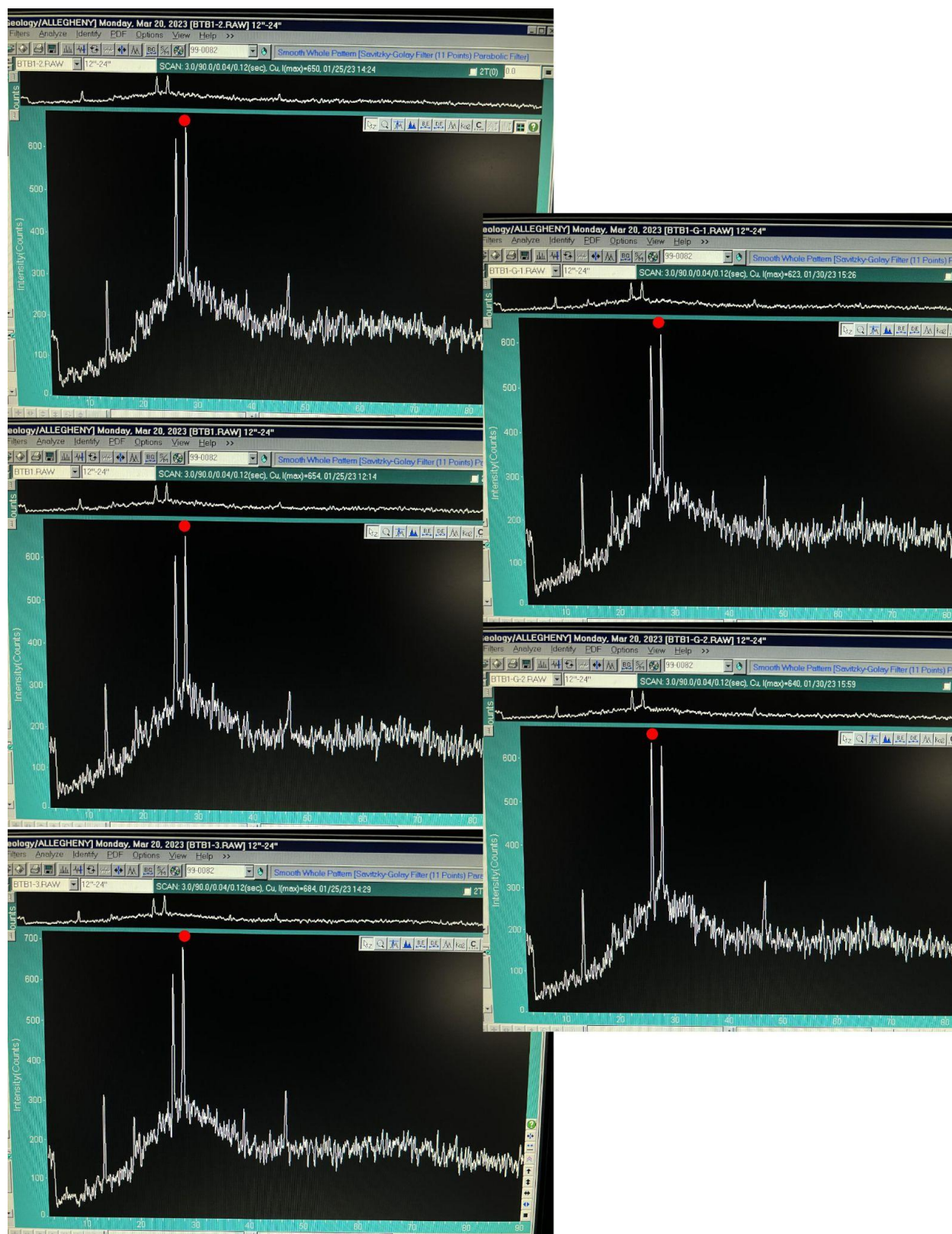


Figure 11.2. Raw XRD data charts of Sample Btb1, red dot indicates primary peak (raw trials 1, 2, 3 from top down on left, ethylene glycol treated trials 1, 2 from top down on right).



Figure 11.3. Raw XRD data charts of Sample Btb2, red dot indicates primary peak (raw trials 1, 2, 3 from top down on left, ethylene glycol treated trial 1 on right, other EG trial was lost).

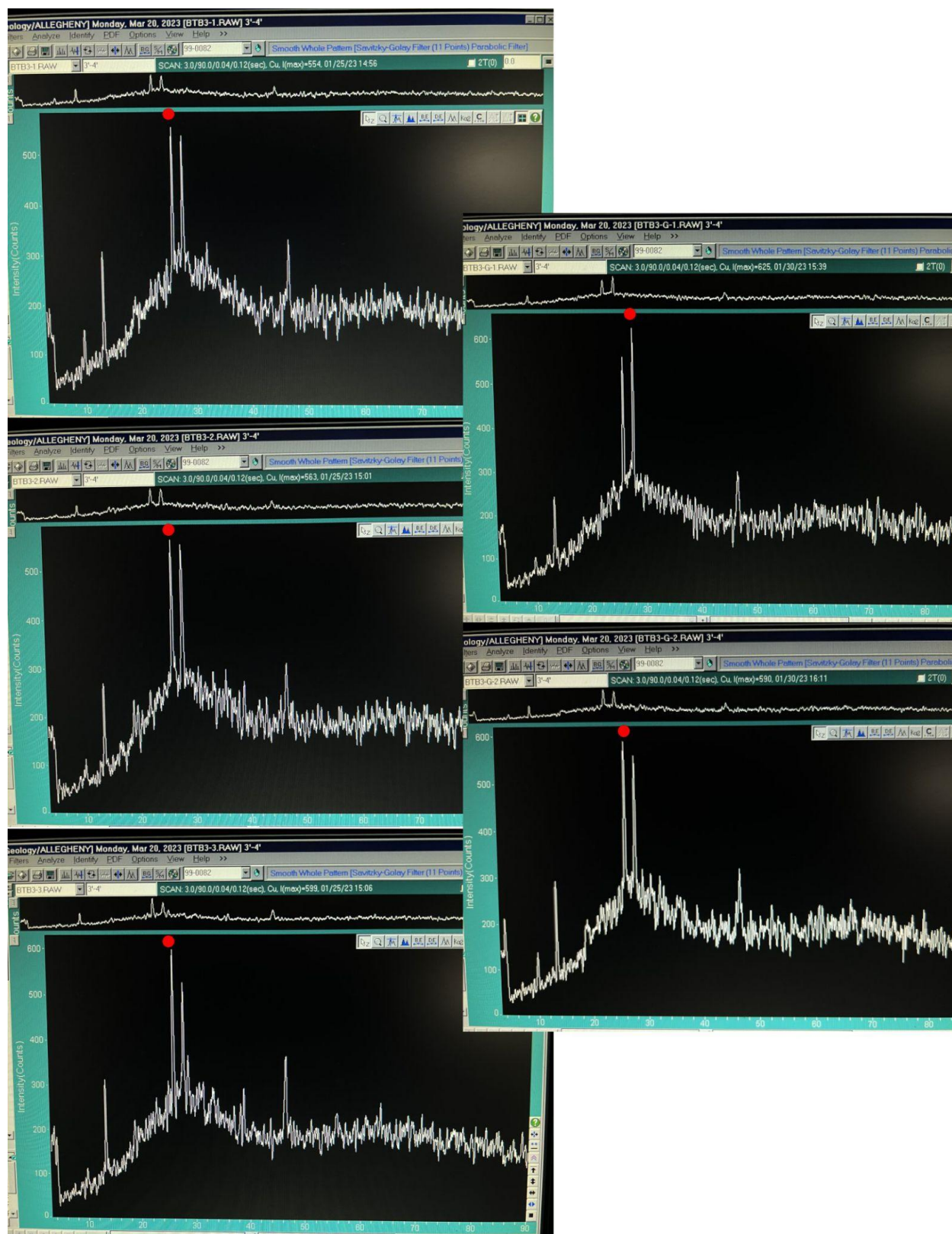


Figure 11.4. Raw XRD data charts of Sample Btb3, red dot indicates primary peak (raw trials 1, 2, 3 from top down on left, ethylene glycol treated trials 1, 2 from top down on right).

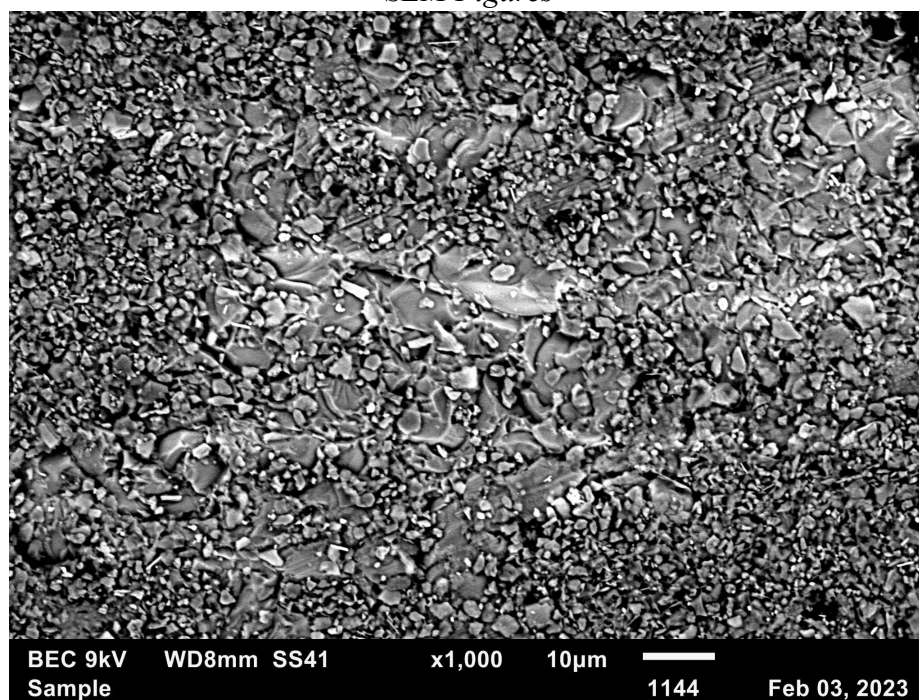
*SEM Figures*

Figure 12.1. Sample Eb1 image in BSE depicting differences in isolated clay grain sizes and grain boundaries as well as underlying textures.

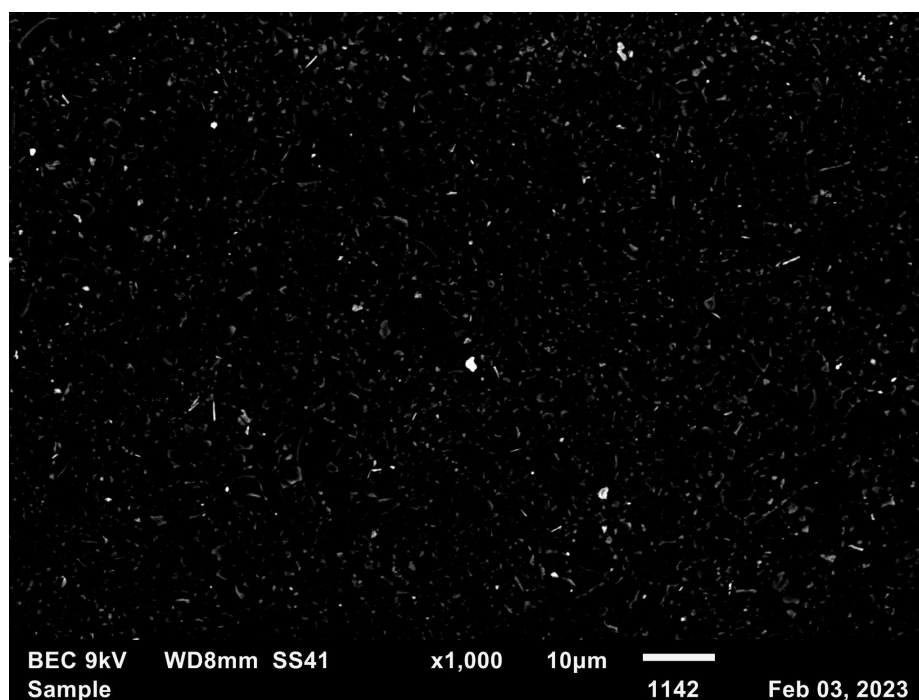


Figure 12.2. Sample Eb1 image in BSE depicting overall mineral weights of isolated clay (brighter = heavy minerals, darker = light minerals).



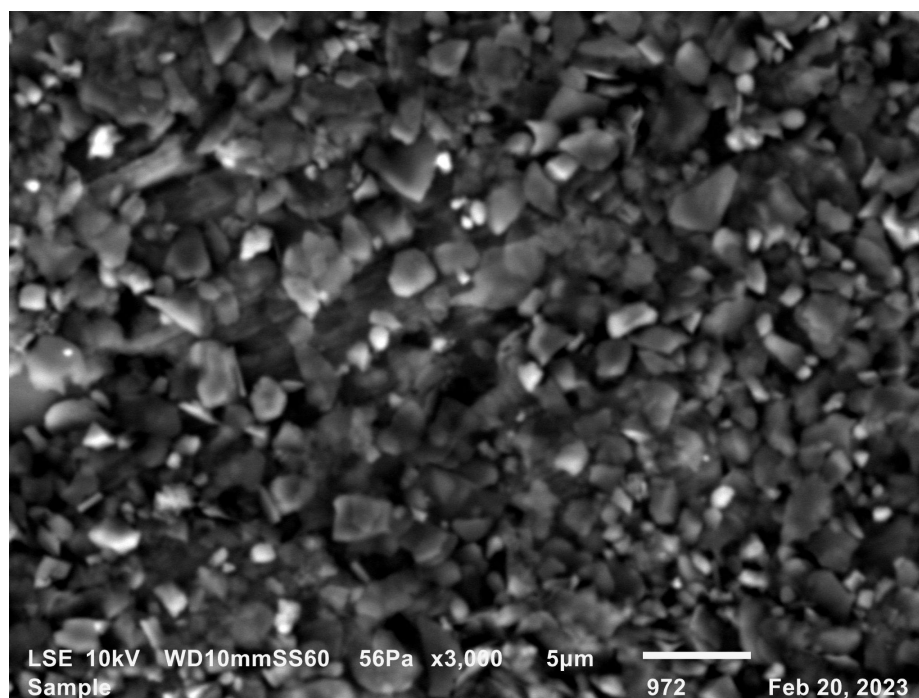


Figure 12.3. Sample Eb1 image in LSE depicting isolated clay grain boundaries and grain sizes.

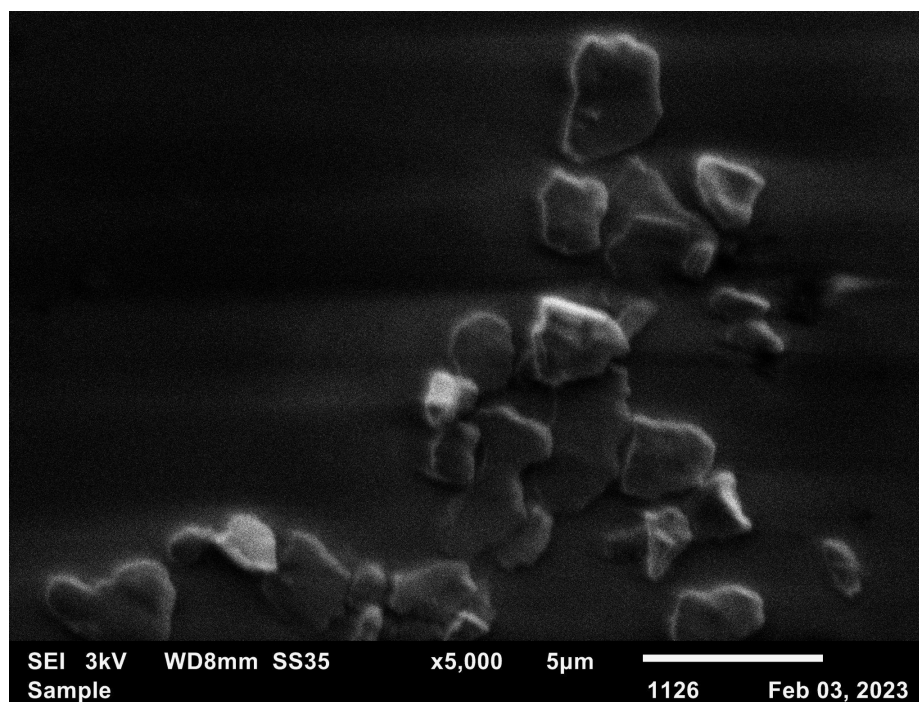


Figure 12.4. Sample Btb1 image in SEI depicting distinct isolated clay grain boundaries and subangular grains.

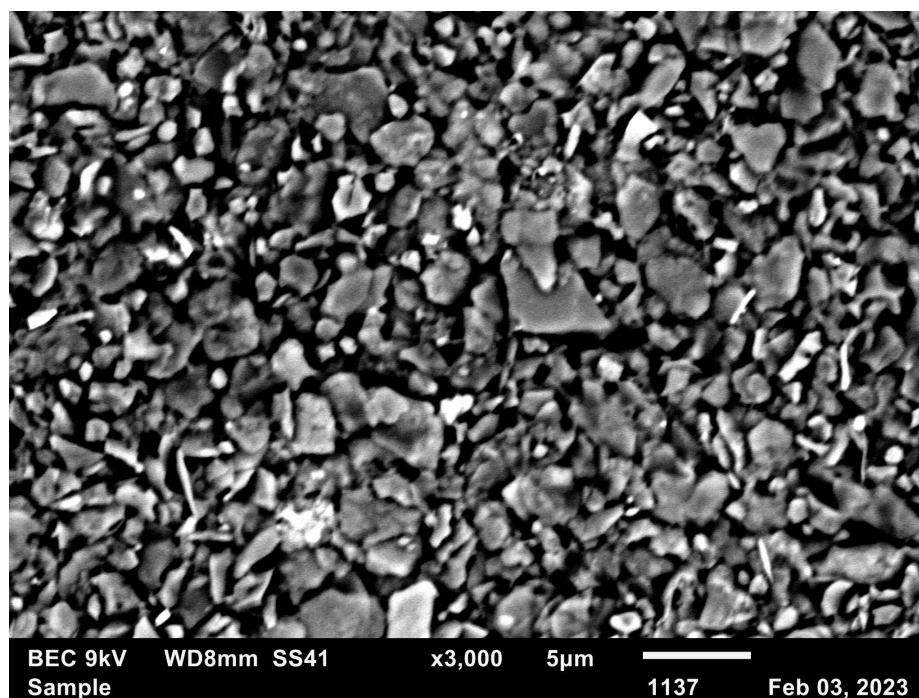


Figure 12.5. Sample Btb1 image in BSE depicting isolated clay grain boundaries and differing grain sizes.

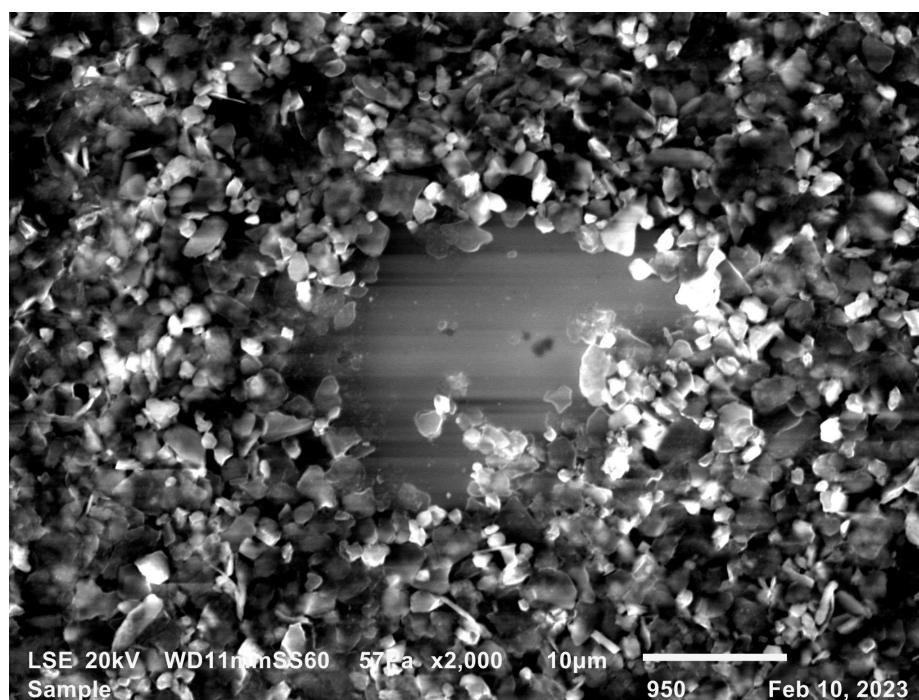


Figure 12.6. Sample Btb2 image in LSE depicting isolated clay grain boundaries and grain sizes around an empty space on the glass sample slide.

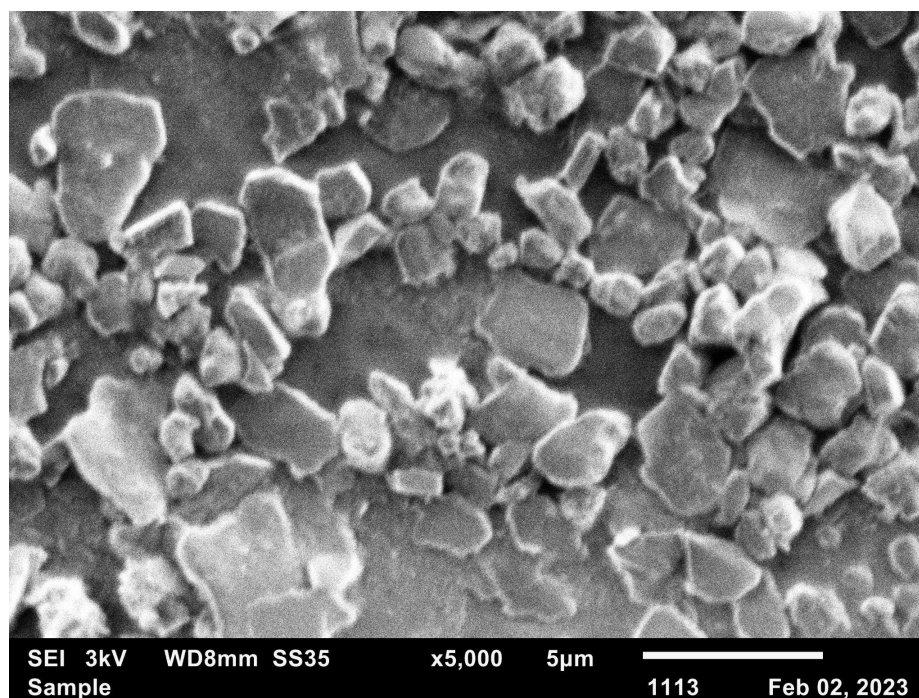


Figure 12.7. Sample Btb2 image in SEI depicting isolated clay subangular grain boundaries and different grain sizes.

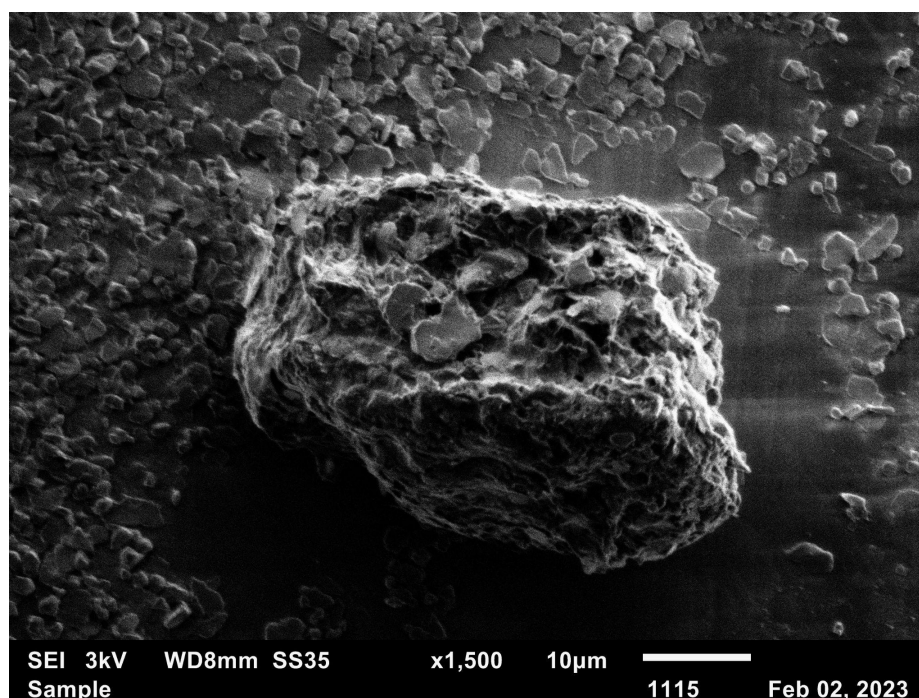


Figure 12.8. Sample Btb2 image in SEI depicting a large, preserved grain of isolated clay around other smaller clay grains.

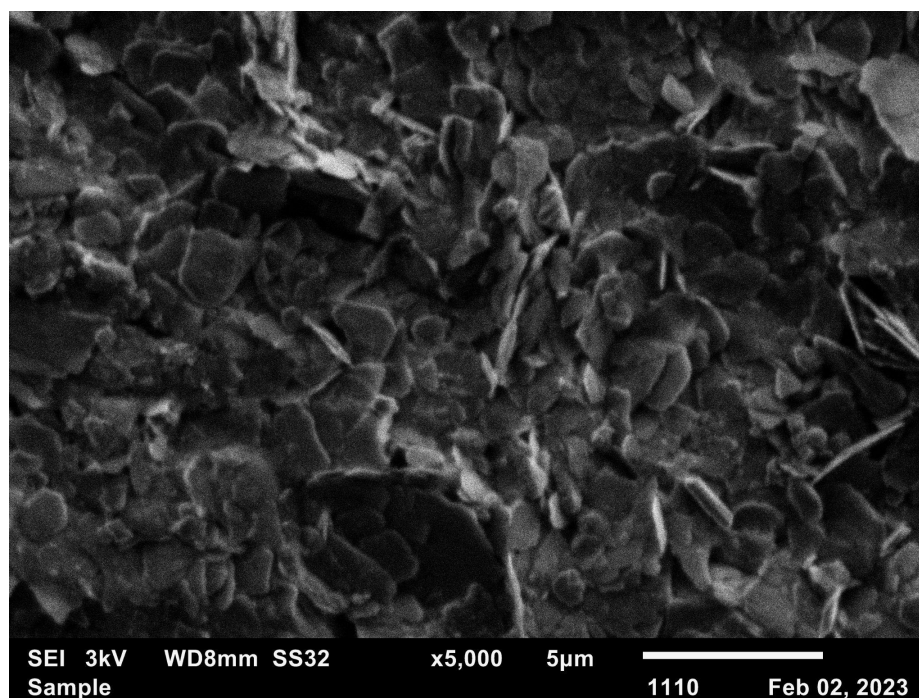


Figure 12.9. Sample Btb3 image in SEI depicting the isolated clay grain size and shape as well as depositional structures, including clay grains oriented perpendicular to the rest of the matrix.

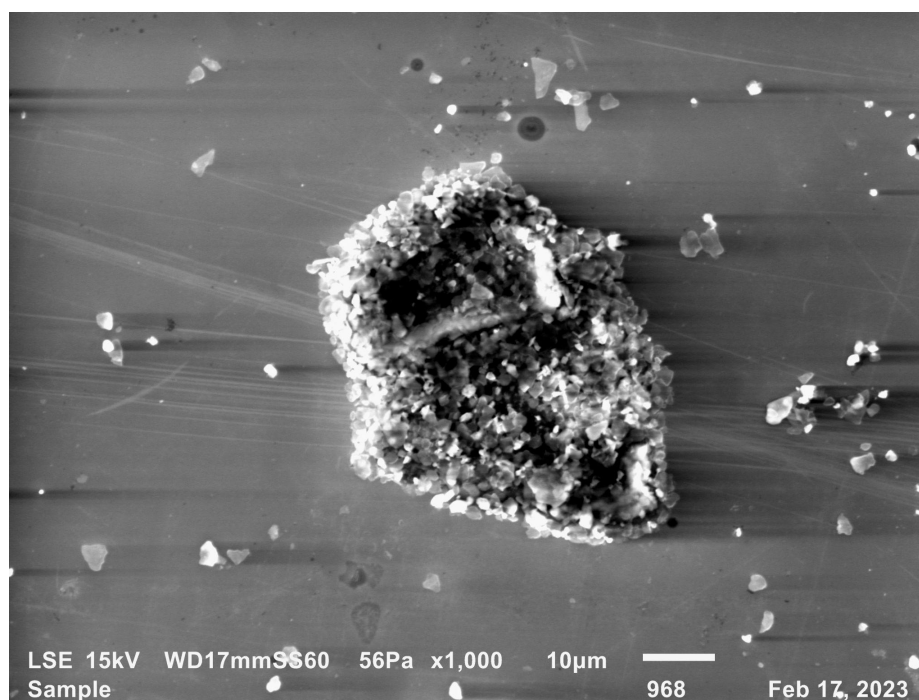


Figure 12.10. Sample Btb3 image in LSE depicting a large, preserved isolated clay grain on an empty space of the glass sample slide.

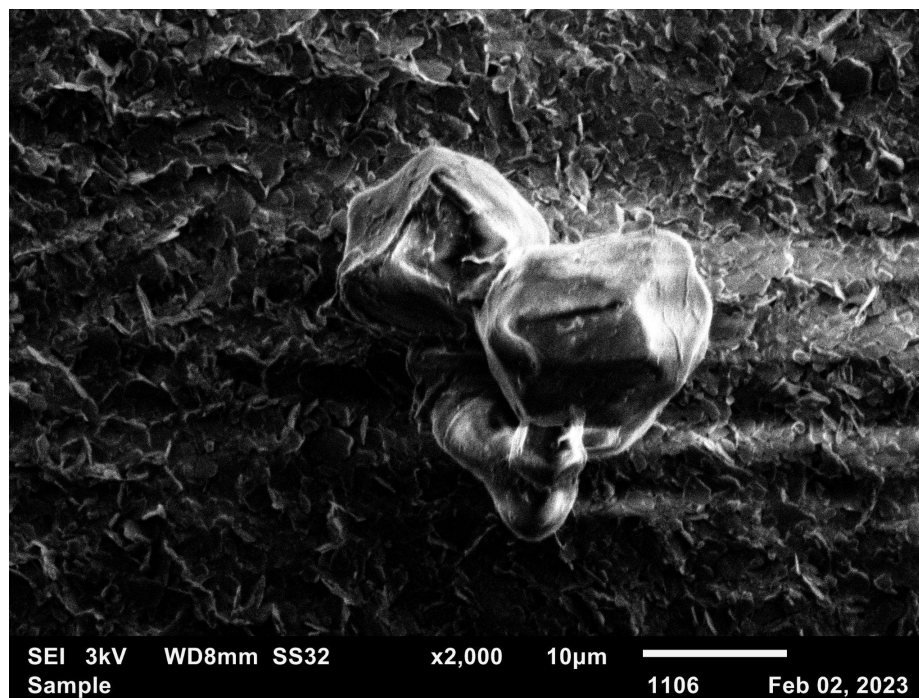


Figure 12.11. Sample Btb3 image in SEI depicting a preserved cluster of an unidentified grain, all on top of isolated clay grains which form a fabric of grain boundaries.



*EDS Figures*

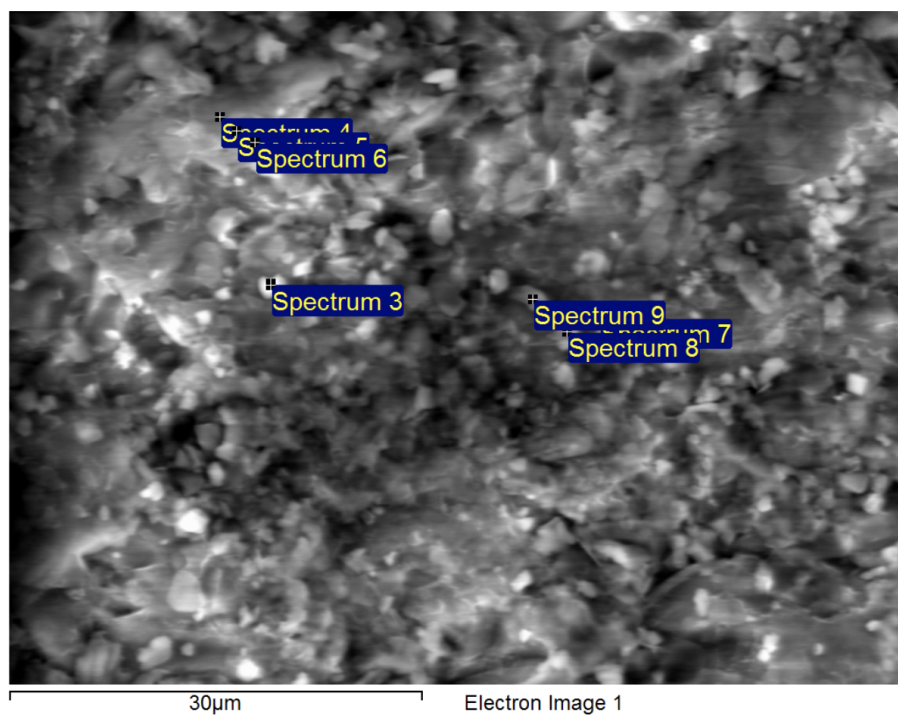


Figure 13.1. Sample 1 (Eb1) EDS location of spectrums on sample image

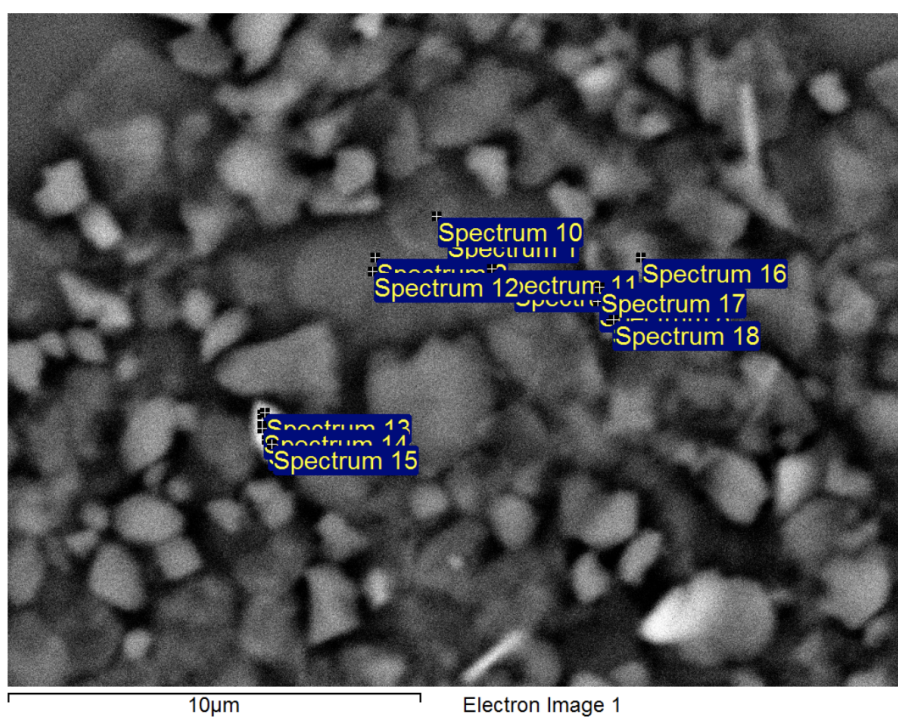


Figure 13.2. Sample 2 (Btb1) EDS location of spectrums on sample image (Label Substitution: Spectrum 10 = Spectrum 1, ..., Spectrum 18 = Spectrum 9)

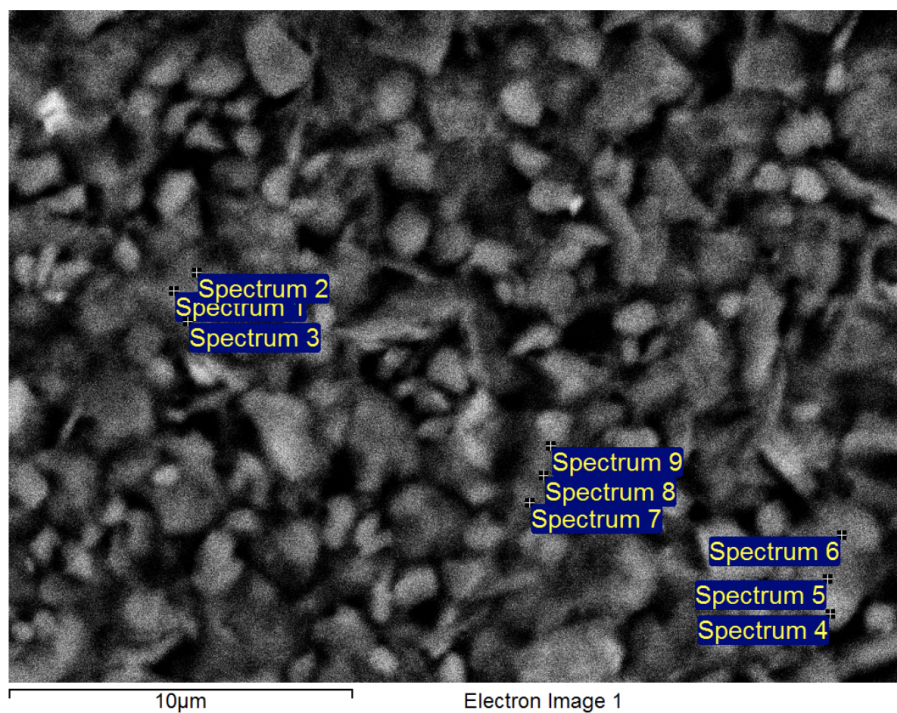


Figure 13.3. Sample 3 (Btb2) EDS location of spectrums on sample image

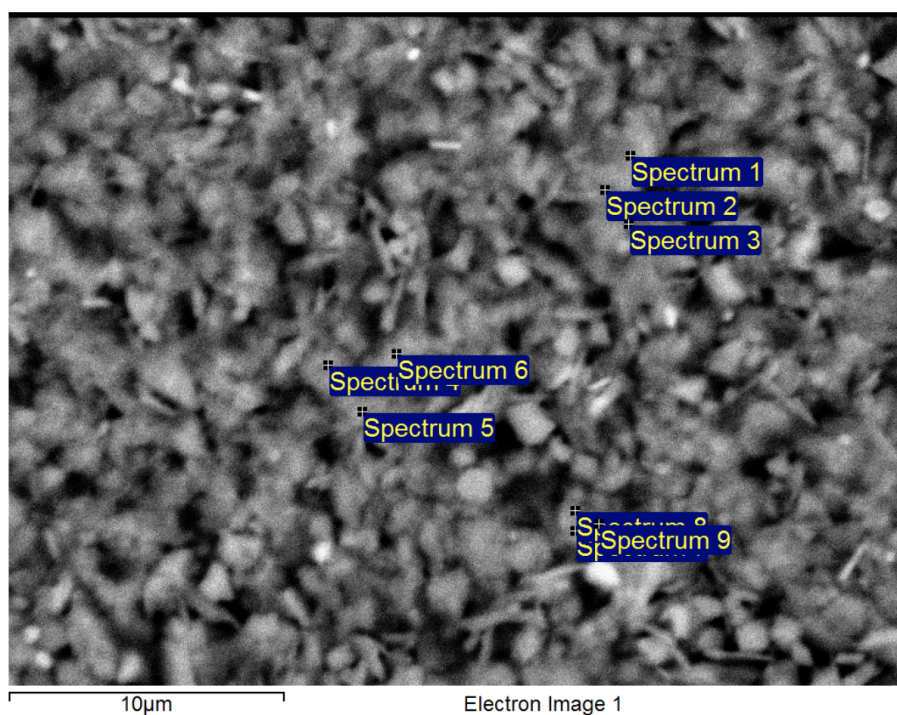


Figure 13.4. Sample 4 (Btb3) EDS location of spectrums on sample image