

CLAY MINERALS IDENTIFICATION BY X-RAY POWDER DIFFRACTION NEAR A MINING SITE, MALAYSIA

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Abstract

The soil samples collected from an agricultural region near the Sungai Chalit mine site in Raub, Pahang, Malaysia were subjected to X-ray powder diffraction (XRPD) analysis for the first time. The PanAnalytikX'pert Pro XRD equipment at the XRD laboratory, Material Technology, Nuclear Malaysia, was used to identify the clay minerals present in the samples. After thorough analysis of all samples, it has been determined that microcline is found in every sample, whereas bytownite has been detected in just three unique samples (DS2, DS15, and DS17). Two discrete variants of zeolite were discerned in two specimens, denoted as DS2 and DS17. Sample DS6 contains kaolinite. Sample C13 comprises four clay minerals: microcline, anorthite, birnessite, and tremolite. The occurrence of microcline in soil signifies the erosion of rocks abundant in feldspar, such as granite, resulting in a reduction of essential minerals like potassium and calcium. This depletion has the potential to affect plant nutrition and crop yield.

Key words: X-ray powder diffraction, Clay minerals, Agricultural soil.

Introduction

Clay minerals play a crucial role in the formation of soil formations. For instance, Garrels and Mackenzie's research in 1971 found that the percentage of clay minerals in sedimentary rocks is around 35% by weight. The soil composition consists of around 20-30% air in the pore space, 20-30% water, and 45-50% mineral soil solids, with 1-5% organic matter (Weaver & Pollard, 1975). The unique structures and surface properties of clay minerals, such as swelling, cation exchange capacity, and solid acidity, have been found to affect the characteristics of soils and rocks. This has been demonstrated in various studies (Moore and Reynolds, 1997; Okada *et al.*, 2006; Yuan *et al.*, 2008, 2009; Środoń and McCarty, 2008; Fan *et al.*, 2009; He *et al.*, 2010; Liu *et al.*, 2011, 2013, Zhou *et al.*, 2018; Ali *et al.*, 2022; Keya *et al.*, 2023).

X-ray diffraction (XRD) has become increasingly important as an analytical method for studying natural clay materials over the past century. It is used to qualitatively and quantitatively examine these materials. Various researchers have contributed to the development of XRD, including Taylor in 1978, Bish and Howard in 1988, Bish and

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Chipera in 1994, Środoń in 2002, and Chipera and Bish in 2013. A crucial concern in the domain of mineral analysis, especially when dealing with clay minerals, is the precise evaluation of quantity.

The many characteristics of clay minerals, such as their broad variety of chemical compositions, preferred orientation, structural disorder, and major structural changes, are the main reasons for this (Hillier, 2000; Środoń *et al.*, 2001; Środoń, 2002, 2013; Bergaya *et al.*, 2006). Quantifying clay minerals is more challenging compared to quantifying other minerals due to the distinctive structures they possess, including different polytypes and types of flaws. Additionally, clay minerals may vary in terms of chemical composition and the influence of preferred orientation (Środoń, 2002). The alignment and orientation of clay mineral particles influences the X-ray diffraction (Brindley, 1980; Moore *et al.*, 1997) intensity of powdered samples. Nevertheless, the majority of clay mineral particles have a flat, plate-like structure. Commonly used preparation techniques, such as front-loading, tend to result in the alignment of clay minerals in a desired orientation (Hillier, 1999). The XRD reflection intensities of clay minerals are often amplified by the preferred orientation, as observed by Lippmann in 1970. Consequently, the preferred orientation is considered a significant source of mistake in the quantitative analysis of clay minerals, as stated by Środoń *et al.* in 2001.

In the past, qualitative phase analysis, quantitative phase analysis using calibration techniques, and crystal structure determinations were separate fields of study. The Rietveld approach emerged as the primary technique for quantitative phase analysis (QPDA) in the late 20th century (Rietveld, 1967, 1969), replacing older methods. Subsequently, quantitative phase analysis has necessitated the use of crystal structures and fitting instead of calibrations. Simultaneously, the number of reference patterns for phase identification grew as crystal structure data was included, and databases were quickly populated with reference powder patterns derived from single crystal structure data. The software's primary objective is to perform phase identification, which serves as the first stage in X-ray diffraction (XRD) powder analysis. The user has the ability to do identification by analyzing the peak locations (d spacing and relative intensities) and/or by examining the whole net profile of the experimental pattern.

However, often using both strategies yields optimal outcomes, including significant and minor stages. For a search-match job, it is advantageous to merge many commercial reference databases (Allen *et al.*, 1987; Belsky *et al.*, 2002; Villars *et al.*, 2002, 2004; Downs and Hall-Wallace, 2003; Gražulis *et al.*, 2009, 2012; ICDD) together with user databases. Consequently, contemporary powder pattern analysis software must not only manage peaks, background, profile, and reference data, but also accommodate crystal structures, enable space group transformations, and facilitate various fits, as well as support related methods like microstructure analysis. Emerging one and two dimensional detectors provide expedited and enhanced data acquisition, necessitating the use of statistical

techniques and a preliminary identification of "noteworthy" data for further analysis. Automation and data throughput have grown in significance at the same time (Degen *et al.*, 2014). The objective of the study was to identify the clay minerals present in the samples by utilizing X-ray powder diffraction. The minerals were identified by employing the diffraction pattern peaks and peak positions obtained from the inorganic crystal structures database (ICSD) of FIZ Karlsruhe, followed by analysis using the Rietveld refinement in HighScore software of PANalytical. The quality of analysis were ensured by Material Technology Division, Malaysia Nuclear Agency.

Method and Material

i) Principle of X-ray Diffraction

X-ray diffraction is the phenomenon where X-rays are dispersed by atoms that are organized in a regular pattern inside crystals. The atoms act as scattering centers (Moore and Reynolds, 1997), producing X-rays in all directions at the same wavelength as the incoming radiation (coherent scattering). The atoms' organized configuration causes the X-rays to disperse in a pattern where they are synchronized in some directions determined by the crystal's symmetry and atomic distances, while they are unsynchronized in all other directions (Figure-1).

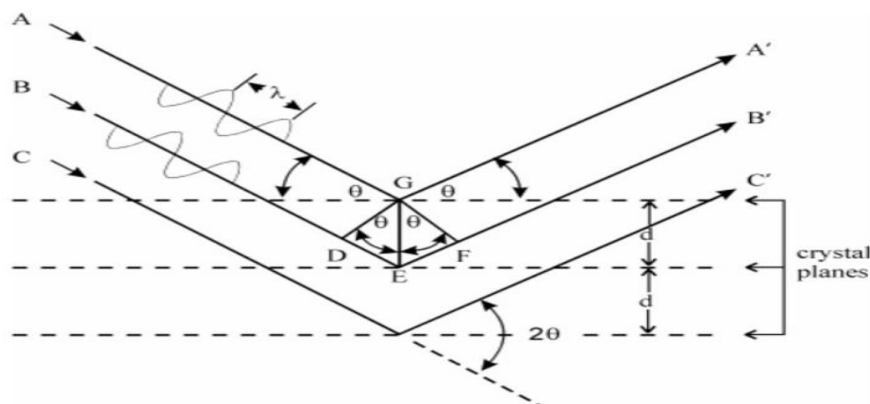


Fig. 1. Diagram illustrating X-ray diffraction (XRD) using evenly spaced atomic planes inside a crystal.

The distance between a given set of planes is termed d-spacing. The d-spacing, although on a scale of Angstroms, can be determined quite accurately using XRD. The principles underlying this determination are elegantly expressed by the Bragg equation: $n\lambda = 2d \sin \theta$;

where n is an integer, λ is wavelength of the radiation, d is d-spacing, and θ is the angle between the planes and the incident X-ray beam.

The factor in the Bragg equation of interest to mineralogists is the d-spacing, which can be determined in XRD analysis by fixing λ and measuring the θ angle where a peak in X-ray intensity occurs.

ii) Sample Collection and preparation

Five soil samples were collected from Sungai Chalit, Raub, Pahang, Malaysia, for the purpose of identifying and analyzing the structure of clay minerals. The samples were prepared for X-ray diffraction (XRD) examination after conducting element analysis using X-ray fluorescence (XRF). X-ray diffraction (XRD) is mostly used for the identification of various compounds based on their diffraction patterns or diffractograms, making it the most often employed application of XRD (Zwell *et al.*, 1975; Chipera *et al.*, 2013; Salma *et al.*, 2023 Wasel *et al.*, 2023).



Fig. 2. Soil samples for clay mineral analysis.

Before doing XRD measurements, it is crucial to adequately prepare the sample. The XRD sample preparations were carried out using standard techniques. The five samples were oven dried and subsequently crushed using a mortar and pestle. After the grinding operation, dry sieving was conducted. Consequently, a filter size of 500 microns was employed. Only samples less than 500 microns were collected and appropriately labeled. The sample preparation method involved using many pieces of equipment, including the cover glass, PW 1172/01 sample holder with a back plate, and slide glasses. The powder sample was placed into the holder, which was connected to the back plate. A shard of glass was employed to compact the powder. The surplus was removed by employing a glass plate, thereby prepared the sample for measurement (Figure 3).

iii) X-ray powder diffraction of samples

The PanAnalytikX'pert Pro XRD equipment (Figure 4) at the XRD laboratory, Material Technology, Nuclear Malaysia, was used to examine all samples. The inputted scan settings were as follows: The scan axis is set to Gonio. The start position is $10.0297^{\circ}2\theta$, the end position is $79.9567^{\circ}2\theta$, and the step size was $0.0330^{\circ}2\theta$. The scan step duration was 19.4436 seconds, and the scan type was PSD (2.12). The divergence slit was set at a fixed value of 0.50 for all specimens with a length of 10 mm. The anode material used for the measurement in this X'pert Pro XRD instrument was copper (Cu), with specific wavelengths of K-Alpha1 (1.54060 \AA), K-Alpha2 (1.54443 \AA), K-Beta (1.39225 \AA), and a ratio of K-A2 to K-A1 of 0.50000. The generator was tuned to a current of 30 milliamperes and a voltage of 40 kilovolts for all diffraction investigation.

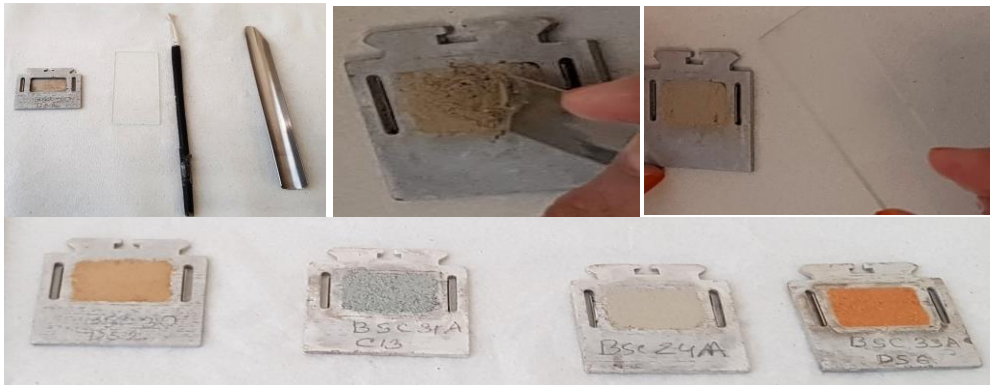


Fig. 3. Sample preparation for XRD measurement.

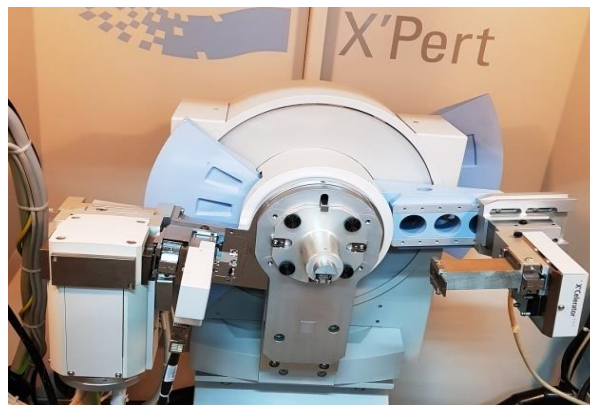


Fig. 4. PANalytical X'Pert PRO XRD system at MTEG.

iv) Data Processing

Subsequently, all diffractograms underwent processing, refinement, and comparison with the powder diffraction file (PDF) using High Score suite, PANalytical's own program for analyzing powder diffraction. This tool enables users to conduct a wide range of crystallographic experiments, including the capability to determine crystal structures using powder diffraction data. The program employed qualitative phase identification, profile fits, and phase rietveld fits to perform quantitative determinations (Zhou et al., 2018). In addition, it was utilized for graphical comparisons, resolving inorganic crystal structures, identifying unit cells, and conducting statistical analyses to verify the presence of certain clay minerals (Degen *et al.*, 2014).

Result and discussion

The diffraction pattern of sample C13 in Figure 5 shows the existence of Anorthite, Birnessite, Microcline, and Tremolite. Anorthite is a very prevalent mineral that has a distinct, pointed appearance. It consists of a crystalline material. The sample's quantitative composition was determined using the rietveld refinement process, which identified the presence of Anorthite (56.2%), Birnessite (1.9%), Microcline (7.2%), and Tremolite (34.7%). Hence, Anorthite and Tremolite have greater importance in comparison to other minerals, accounting for 56.2% and 34.7% respectively.

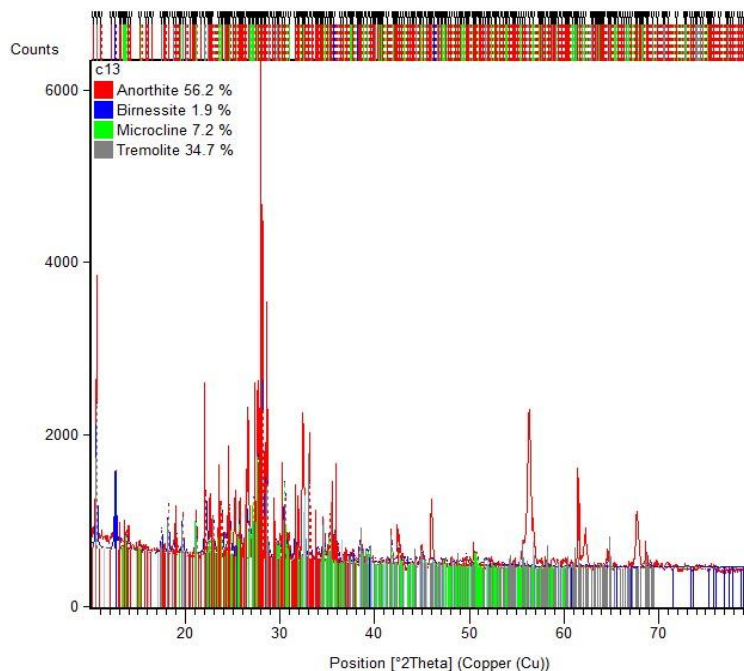


Fig. 5. XRD diffractogram of sample C13. (2θ vs Counts).

The diffraction pattern of sample DS2 in Figure 6 indicates the existence of Microcline, Bytownite, and Zeolite SIZ-7. Microcline is more prevalent than other minerals and has a distinct cleavage. The sample contains Microcline (56.1%), Bytownite (24.7%), and Zeolite SIZ-7 (19.2%). Hence, Microcline and Bytownite exhibit notable prominence in comparison to other minerals, accounting for 56.1% and 24.7% respectively.

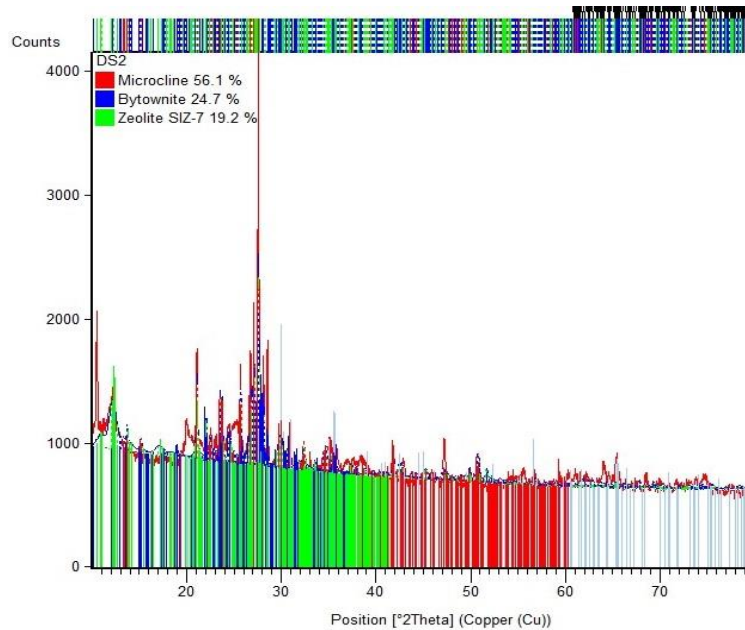


Fig. 6. XRD diffractogram of sample DS2. (2θ vs Counts).

The diffraction pattern of sample DS6 in Figure 7 indicates the existence of Microcline and Kaolinite 1A. Kaolinite 1A is the most prevalent mineral and has a distinct fracture. It consists of a crystalline material. The composition of the sample consists of Microcline (25.4%) and Kaolinite 1A (74.6%). Thus, Kaolinite 1A has more importance in comparison to Microcline.

The diffractogram of sample DS15 in Figure 8 indicates the existence of Microcline and Bytownite. Both Microcline and Bytownite possess a distinct cleavage and were made of crystalline matter. Microcline (41.1%) and Bytownite (58.9%) are the constituents of the sample.

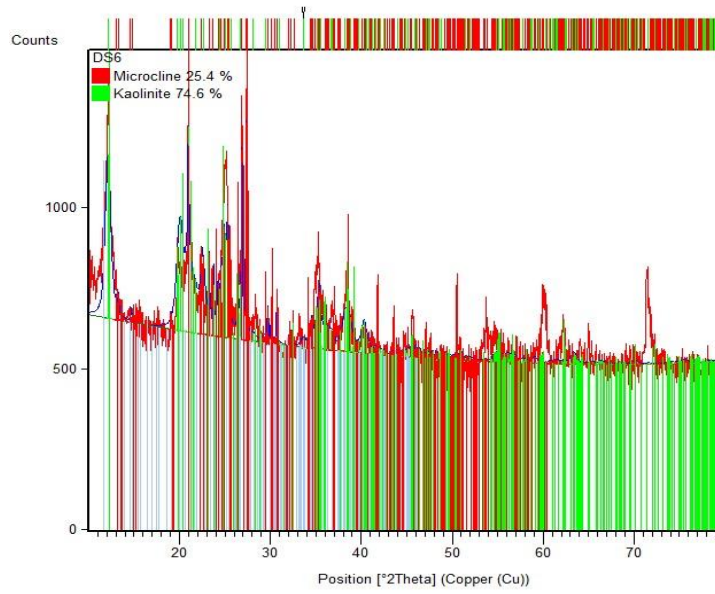


Fig. 7. XRD diffractogram of sample DS6. (2θ vs Counts).

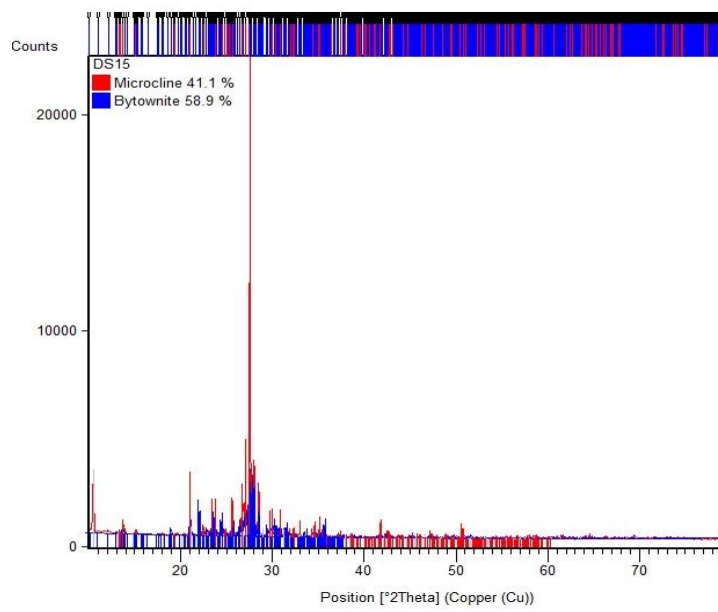


Fig. 8. XRD diffractogram of sample DS15. (2θ vs Counts).

Figure 9 displays the diffractogram of sample DS17, indicating the existence of Microcline, Bytownite, and Zeolite. Minerals has a distinct and pointed beak. It consists of a crystalline material. Microcline (35.5%), Bytownite (27.2%), and Zeolite A (39.3 %) are the minerals found in the sample. Hence, Microcline and Zeolite A exhibit greater importance in comparison to other minerals, accounting for 35.5% and 39.3% respectively.

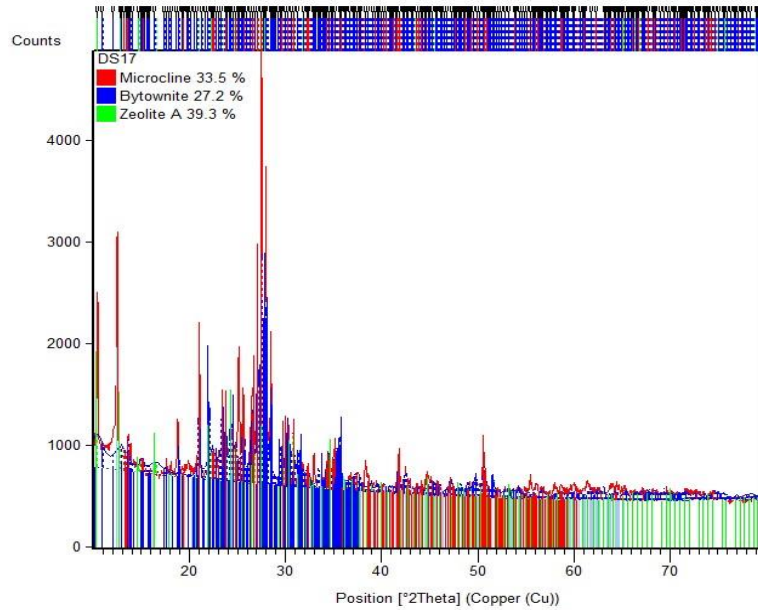


Figure 9: XRD diffractogram of sample DS17. (2θ vs Counts).

Minerals found in samples named C13, DS2, DS6, DS15 and DS17 with their ICSD reference and chemical formula are stated in table 1. Microcline has been identified in all samples, whereas Bytownite has only been recognized in three distinct samples (DS2, DS15, and DS17). It may be deduced from the presence of microcline in soil that feldspar-rich rocks such as granite have been worn. Minerals composed of feldspar are sensitive to the chemical weathering process, which is initiated when water and carbon dioxide combine to generate carbonic acid. Potassium, sodium, and calcium all dissolve as a result of the reaction between carbonic acid and feldspar. This causes the components in the soil to become more mobile, where they may be carried away by runoff, rivers, and the ocean. Two distinct forms of zeolite were identified in two samples, referred to as DS2 and DS17.

Table 1. Minerals found in samples with ICSD reference.

Sample Name	ICSD Ref. Code	Compound Name	Chemical Formula
C13	98-001-7945	Anorthite	Al ₂ Ca ₁ O ₈ Si ₂
	98-002-8787	Birnessite	H ₃ Mg _{0.29} Mn ₂ O _{5.5}
	98-001-7678	Microcline	Al _{0.99} K _{0.94} Na _{0.06} O ₈ Si _{3.01}
	98-001-2569	Tremolite	H ₂ Al _{0.29} Ca _{1.69} Fe _{0.49} Mg _{4.6} Na _{0.11} O ₂₄ Si _{7.82}
DS2	98-001-7357	Microcline	Al ₁ K ₁ O ₈ Si ₃
	98-001-7029	Bytownite	Al _{1.94} Ca _{0.85} Na _{0.14} O ₈ Si _{2.06}
	98-008-5669	Zeolite SIZ-7	Al _{19.2} Co _{12.8} O ₁₂₈ P ₃₂
DS6	98-004-5844	Microcline	Al ₁ K _{0.95} Na _{0.05} O ₈ Si ₃
	98-002-1819	Kaolinite 1A	H ₄ Al ₂ O ₉ Si ₂
DS15	98-001-7357	Microcline	Al ₁ K ₁ O ₈ Si ₃
	98-001-7029	Bytownite	Al _{1.94} Ca _{0.85} Na _{0.14} O ₈ Si _{2.06}
DS17	98-001-7357	Microcline	Al ₁ K ₁ O ₈ Si ₃
	98-001-7029	Bytownite	Al _{1.94} Ca _{0.85} Na _{0.14} O ₈ Si _{2.06}
	98-004-0992	Zeolite A	H ₂₂ Al ₁₂ Co ₄ Na ₄ O ₄₈ S ₁₁ Si ₁₂

Only the DS6 sample has kaolinite in its composition. Kaolinite, are formed when the residual components of feldspar, such as aluminum and silica, are exposed to heat and pressure. According to Bell (n.d.), clay minerals are essential to the structure and fertility of the soil because of their ability to store water and nutrients and to offer a home for soil bacteria. The C13 sample consists of four clay minerals: microcline, anorthite, birnessite, and tremolite. Mineral identification relies on the measurement of d-spacings and the comparison of relative peak intensities. Every material produces many diffraction peaks. Identification becomes significantly easier when the sample contains only a single mineral. The presence of many minerals in a mixture can result in intricate XRD patterns, making it difficult to identify the individual minerals (Ruan & Ward, 2002). Nevertheless, there are various aspect that partially alleviate the difficulty for soils. The majority of soils consist of a limited number of minerals, which tend to divide into different particle size groups. These groups are often examined individually using X-ray fluorescence (XRF) analysis in order to simplify the analysis process (Arefin et al., 2018). In addition, the minerals that are found in soil on a regular basis make up only a small portion of the more than 40,000 different minerals that have been discovered.

Conclusion

The presence of microcline in soil is evidence of the weathering of rocks rich in feldspar, such as granite, which has led to a depletion of important minerals like potassium and calcium. The depletion of this resource has the potential to have an impact not just on the yield of crops but also on the nutrients that plants get.

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