Chapter

Clay Mineral Identification Using X-Ray Diffraction

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Abstract

This chapter presents a comprehensive overview of clay mineral characterization using X-ray diffraction (XRD), a fundamental analytical tool widely applied in geosciences, environmental studies, and planetary science. It begins by outlining the theoretical principles of XRD, including Bragg's Law, and details essential methods for clay sample preparation, such as oriented mounts and treatments like glycolation and heating, which aid in distinguishing between major clay groups. The identification of minerals such as kaolinite, illite, smectite, and chlorite, as well as the detection of mixed layer clays, is thoroughly discussed. The chapter also explores the role of XRD in monitoring mineralogical changes during diagenesis, and microbial interactions. In addition, it highlights the importance of clay mineral detection in Martian surface exploration, where XRD analyses, such as those conducted by the Curiosity rover offer insights into past aqueous activity and habitability. By integrating terrestrial and extraterrestrial case studies, this chapter underscores the broad applicability of XRD in clay science. Building on this foundation, it further examines how XRD-derived mineralogical data inform geotechnical engineering practices, including expansive soil characterization, soil–water behavior modeling, stabilization design, and long-term performance monitoring. Applications in offshore geotechnics, environmental containment, foundation interaction modeling, and GIS-integrated remote sensing are also addressed. These engineering perspectives demonstrate how mineral-level precision enhances design reliability, risk assessment, and infrastructure resilience in clay-rich environments. XRD enables early detection of problematic mineral phases, supports performance-based treatment selection, and improves the predictive accuracy of mechanistic models used in infrastructure design.

Keywords: clay minerals, X-ray diffraction (XRD), smectite, kaolinite, illite, expansive soils, soil stabilization, geotechnical engineering, soil–water characteristic curve (SWCC), mineralogical analysis, environmental containment, offshore geotechnics, remote sensing, infrastructure resilience, Martian mineralogy

1. Introduction

Clay minerals are fundamental components of soil and sedimentary environments, influencing a wide range of geotechnical, environmental, and geological processes. Their unique layer structures, variable chemical compositions, and surface properties govern critical behaviors such as swelling, shrinkage, permeability, shear

strength, and contaminant retention. As a result, accurate identification and quantification of clay minerals are essential for predicting soil performance and designing effective engineering solutions.

Among the various mineral identification techniques, X-ray diffraction (XRD) stands out as the most definitive and widely applied method for characterizing crystalline phases in clays. XRD provides direct insight into mineral structures, enabling the detection of key diagnostic features such as basal spacings, peak intensities, and thermal stability. These characteristics are essential for distinguishing between mineral groups like smectite, kaolinite, illite, and mixed-layer clays. This analytical capability extends across disciplines, supporting both scientific investigations into clay genesis and applied engineering analyses for infrastructure design, hazard mitigation, and environmental management.

This chapter is organized into two complementary sections. Section 2 presents the scientific basis and analytical methods for clay mineral identification using XRD, covering diffraction principles, sample preparation, and pattern interpretation within a geological and geochemical context. Section 3 builds upon this foundation to explore engineering perspectives, illustrating how XRD-derived mineralogical data are integrated into geotechnical design, soil stabilization, performance modeling, and long-term monitoring. Together, these sections provide a comprehensive view of how mineralogical characterization using XRD bridges fundamental science and practical engineering.

2. Scientific basis and analytical methods for clay mineral identification using X-ray diffraction (XRD)

X-ray diffraction (XRD) is a fundamental technique for determining the mineralogical composition of soils, sediments, and rock materials in geological and geochemical studies. By analyzing the diffraction patterns generated when X-rays interact with a crystalline lattice, it is possible to determine structural parameters such as interlayer spacings, symmetry, and degree of crystallinity. These parameters allow clear differentiation between smectite, kaolinite, illite, and mixed-layer clays.

This section outlines the principles of diffraction and Bragg's Law, along with key considerations for sample preparation and treatment. Emphasis is placed on interpreting diagnostic peak positions, intensities, and shifts that provide accurate clay mineral identification. These analytical foundations support the engineering applications presented in later sections.

2.1 Principles of X-ray diffraction for clay minerals

X-ray diffraction (XRD) is based on the constructive interference of monochromatic X-rays with a crystalline sample. When X-rays interact with a crystalline lattice, they are diffracted at specific angles in accordance with Bragg's Law: $n\lambda = 2d \sin\theta$. Each clay mineral has a characteristic set of basal spacing values that enable its identification [1, 2]. For instance, kaolinite is characterized by peaks at approximately 7.1 Å for the (001) plane and 3.57 Å for the (002) plane. Illite typically exhibits a strong reflection near 10 Å. Smectite displays an expansion from around 12–15 Å to approximately 17 Å upon ethylene glycolation. Chlorite, on the other hand, is recognized by its distinctive peaks near 14 Å and 7 Å. These diffraction patterns provide a reliable basis for the mineral specific identification of clay phases.

2.2 Sample preparation

Proper sample preparation is critical for obtaining reliable XRD results when analyzing clays. Typically, clays are separated from the bulk rock or soil by isolating the <2 μm fraction [2]. Disaggregation is carried out by dispersing the sample in distilled water with sodium hexametaphosphate (commonly ~5 g/L) as a deflocculant. Particle-size separation is then achieved by settling based on Stokes' Law to isolate the clay-size fraction. The separated clay suspension is used to prepare oriented mounts on glass slides, which enhance basal reflections and improve mineral identification. Depending on the experimental design, slides are either air-dried at room temperature or oven-dried at ~40–50°C to maintain clay structural integrity. To further distinguish between clay minerals such as smectite, illite, chlorite, and kaolinite, additional treatments are applied: air-drying, ethylene glycolation, and heating to 550°C [3].

2.3 Interpretation of XRD patterns

Interpreting XRD patterns involves recognizing the diagnostic basal spacings of clay minerals and understanding how these spacings change under various treatments. Kaolinite typically exhibits a sharp basal reflection at ~7.15 Å that remains unchanged after ethylene glycolation or heating to 550°C. Illite displays a prominent peak near 10 Å, also stable under ethylene glycolation and heating, though partial collapse can occur at higher temperatures if interlayer cations are altered. Smectites, such as montmorillonite, show a basal reflection near 12–15 Å in air-dried conditions, which expands to ~17 Å upon ethylene glycolation and collapses to ~10 Å after heating to 550°C. Chlorite is identified by its basal peak near 14.2 Å, which remains stable under ethylene glycolation but exhibits a distinct 7.1 Å peak that persists after heating, distinguishing it from kaolinite.

As illustrated in **Figure 1** (*adapted from* [2]), the diagnostic basal spacings for common clay minerals can be identified by their characteristic diffraction peaks under different treatments. Careful comparison of observed peaks with reference patterns, in combination with sample preparation history, ensures accurate mineral identification and helps prevent misinterpretation caused by mixed-layer minerals or preferred orientation effects.

2.4 Applications in geobiology and geochemistry

Clay minerals play a central role in geobiological and geochemical processes due to their high surface area, reactivity, and ability to sorb cations, organic matter, and trace metals. X-ray diffraction (XRD) is essential for identifying mineralogical changes that reflect environmental conditions, microbial activity, and diagenetic transformations.

2.4.1 Paleoenvironments and weathering indicators

Clay mineral assemblages serve as sensitive indicators of paleoclimatic conditions and weathering regimes [4]. For instance, a high abundance of kaolinite typically reflects intense chemical weathering in warm, humid climates [5]. In contrast, illite is commonly associated with physical weathering processes and the presence of cooler climatic conditions. Smectite, on the other hand, often forms in

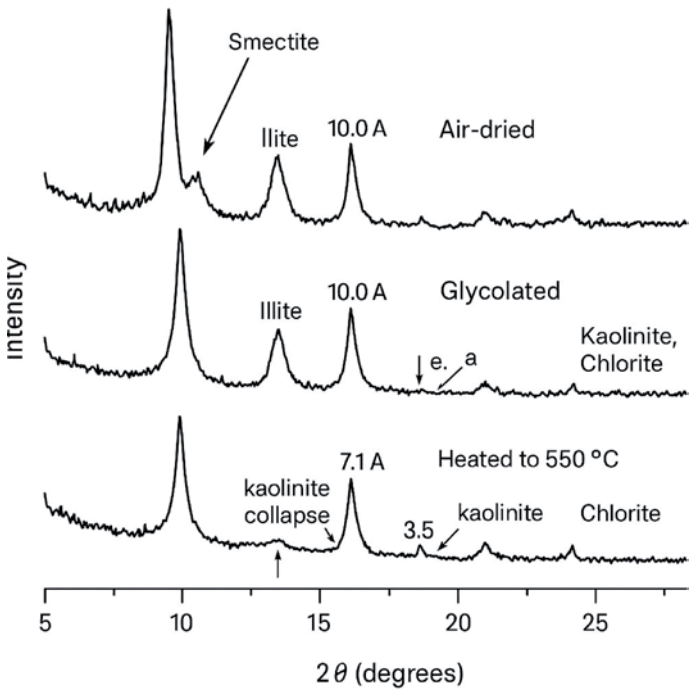

Figure 1.
X-ray diffraction (XRD) patterns of clay samples under different treatments: air-dried, glycolated with ethylene glycol (EG), and heated to 550°C. Diagnostic basal reflections are shown for common clay minerals: the ~12 Å peak that expands to ~17 Å after EG treatment confirms the presence of smectite; the stable 10 Å reflection indicates illite; the 7.1 Å peak that collapses upon heating identifies kaolinite; and the persistence of a 7 Å peak after heating indicates chlorite. The label "a" refers to the basal spacing (d-spacing) of the strongest (001) reflection in angstroms (Å), while "e" denotes ethylene glycol treatment. These phase changes reflect interlayer expansion and thermal stability, which are key criteria for clay mineral identification.

semi-arid environments characterized by poor drainage. XRD analysis of sediment cores enables reconstruction of past environmental changes, especially in lacustrine and marine contexts, providing insight into Quaternary climate fluctuations and provenance.

2.4.2 Microbe: Clay interactions

In geobiology, interactions between microorganisms and clay minerals play a key role in mineral transformations, redox cycling, and biosignature formation in both modern and ancient environments. Iron-rich clays, like nontronite (Fe(III)-smectite) are highly susceptible to microbial reduction under anoxic conditions.

Dissimilatory iron-reducing bacteria (DIRB), such as *Shewanella oneidensis* and *Geobacter sulfurreducens*, oxidize organic substrates while reducing structural Fe(III) in clays. Thereby using the mineral itself as an electron acceptor [6–9]. This process produces Fe(II), which can alter basal spacings (e.g., ~14 Å to ~10 Å), lower crystallinity, and over time drive transformations into secondary minerals such as illite or chlorite [10–12].

These microbial activities leave morphological, structural, and chemical imprints within clays that may persist over geologic timescales. For example, nanoscale lattice changes and mixed-layered phases can be detected using advanced tools like

synchrotron-based XRD and TEM [6, 13]. Such transformations also modify clay surface reactivity, influencing their capacity to adsorb and retain organic matter and thereby enhancing biosignature preservation [14, 15].

Beyond geologic records, these interactions have applied significance. In environmental remediation, DIRB-mediated reduction can immobilize heavy metals and radionuclides [16]. In planetary science, understanding microbe–clay systems inform the interpretation of Martian phyllosilicates and their potential to record traces of ancient life.

2.4.3 Diagenesis and hydrocarbon reservoirs

Clay minerals are highly sensitive to diagenetic transformations that occur during burial. One of the most significant of these is the gradual transformation of smectite into illite, known as illitization. This reaction is strongly influenced by factors such as temperature, potassium availability, and the duration of burial. The smectite to illite transition plays a critical role in petroleum systems, as it directly impacts reservoir properties including porosity, permeability, and the development of overpressure zones [17]. Mixed-layer clays, particularly illite–smectite (I–S) interstratifications, can be analyzed and quantified through XRD techniques to evaluate the thermal maturity of sedimentary basins [3].

2.4.4 Element cycling and environmental geochemistry

Clays play a pivotal role in elemental cycling within soils and sediments due to their capacity to adsorb and exchange a variety of nutrients and contaminants. Their surfaces are highly reactive, allowing for the retention and exchange of essential nutrients such as potassium (K^+) and ammonium (NH_4^+), as well as toxic pollutants like lead (Pb^{2+}) and arsenic (As^{3+}). X-ray diffraction (XRD) serves as a powerful analytical tool to monitor the mineralogical changes that occur during environmental processes, including acid mine drainage, waste stabilization, and interactions between clays and organic matter in soils. For example, smectite, known for its high cation exchange capacity, is particularly effective at binding heavy metals and organic contaminants. Its structural stability and capacity for contaminant retention following environmental treatments can be effectively evaluated through XRD analysis.

2.4.5 Microbial biosignatures in ancient clays

Clay minerals, especially Fe-Mg smectites like nontronite, are especially effective at trapping and preserving organic matter. Their very fine grain size, large surface area and swelling interlayers allow them to adsorb and intercalate organic molecules and metal ions, physically protecting organics from degradation. In ancient sediments and paleosols, layers rich in Fe/Mg–smectite clays often coincide with higher preserved organic carbon [18, 19]. The redox state of a paleosol is the main control on organic retention, with chemically reduced horizons enriched in iron–smectites and amorphous material being especially favorable for biosignatures [18]. In short, Fe-rich clays combine high reactivity with chargeable surfaces, making them excellent matrices for incorporating and preserving microbial organic residues [18, 19].

Furthermore, microbes can transform clay minerals in ways that leave lasting traces. Dissimilatory Fe(III)-reducing bacteria (e.g. *Shewanella*, *Geobacter*) readily use structural Fe(III) in clays as an electron acceptor, producing Fe(II) and breaking

down the clay lattice [16]. Laboratory experiments show that *Shewanella* can reduce a large fraction of the structural Fe(III) in smectite or illite, causing layer collapse and alkali/Al enrichment [20]. This "microbial reductive dissolution" of clays often generates new phases: in situ bioreduction of illite, for example, releases Fe^{2+} into porewaters even at low temperature. Jung *et al.* [21] demonstrated that microbes beneath the Larsen Ice Shelf break down clay-bound Fe(III) and liberate dissolved Fe^{2+}, effectively altering the clay's structure and chemistry [21]. Over time, such reductive processes can drive recrystallization or "illitization" of smectites, as Fe is removed and K/Al in the layers becomes relatively enriched [20].

The mineralogical and geochemical fingerprints of these processes can be preserved as biosignatures. In anoxic, iron-rich sediments, microbial Fe reduction (often coupled to fermentation or methanogenesis) leads to authigenic Fe^{2+}-minerals such as magnetite, siderite ($FeCO_3$) and vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$). Recent work in a ferruginous lake analog (Lake Towuti) shows that framboidal magnetites (primary precipitates) become overgrown by acicular Ni-sulfides (millerite) and by siderite and vivianite during burial, all driven by microbial redox gradients. These phases act as biosignatures of microbial iron and sulfate reduction, fermentation and methanogenesis. In ancient clay-rich rocks (e.g. Archean paleosols or BIFs), such authigenic minerals, together with iron isotopic shifts or enrichments of redox-sensitive trace metals (V, Mo, U) at redox fronts, would mark early microbial activity. In summary, iron-bearing clays not only incorporate organic biosignatures, but their microbially induced alteration products (collapsed lattices, Fe^{2+}-phases, isotopic anomalies) provide a suite of mineralogical and geochemical signatures of past life [18, 19, 22].

2.4.5.1 Mechanisms of biosignature formation

Dissimilatory iron-reducing bacteria (DIRB), particularly species of *Shewanella* and *Geobacter*, play a key role in transforming Fe-bearing clay minerals through redox reactions that leave behind distinct mineralogical and geochemical signatures. These microbes are capable of utilizing structural Fe(III) in the octahedral sheets of smectites such as nontronite as terminal electron acceptors during anaerobic respiration [6, 8, 23]. Upon microbial reduction, Fe(III) is converted to Fe(II), which alters the mineral structure and destabilizes the original lattice. This process frequently results in a measurable collapse of the basal spacing (as detected by X-ray diffraction), along with peak broadening or shifting, indicating clay lattice contraction and mineral reconfiguration [6, 12].

These structural changes are often preserved as biosignatures. Lattice distortions, especially contractions in d-spacing, serve as mineralogical fingerprints of past Fe reducing microbial activity [6, 23]. In some cases, repeated microbial–geochemical cycling can result in interstratification or mixed-layering of clays [3], producing diagnostic XRD patterns not attributable to purely abiotic alteration. Moreover, trace element enrichments (e.g., Mo, Ni, V) that colocalize with Fe reduction zones are increasingly recognized as geochemical biosignatures of microbial metabolism [15]. These trace metals may become incorporated into secondary minerals or adsorbed onto clay surfaces in microbially active zones.

At the microscale, microbial alteration of clay minerals can produce heterogeneity such as zoning, overgrowths, and microtextures surrounding former cell locations. Bishop et al. [24], using high resolution imaging and spectroscopy, observed mineral coatings and zoned clays enveloping fossilized microbial filaments, supporting the

idea that biological processes directly influence mineral morphology during diagenesis [24]. Such microtextures can be exceptionally well preserved in fine-grained clays, especially under rapid burial or anoxic conditions. Altogether, microbial Fe reduction leaves behind a suite of structural, chemical, and textural markers that can function as preserved biosignatures in both modern analogs and ancient clay-rich deposits.

2.4.5.2 Techniques for detection

X-ray diffraction (XRD) is a primary method for detecting microbial alteration in clays by identifying reductions in basal spacings, such as the shift from 14 Å to 10 Å in smectite upon iron reduction, quantifying changes in crystallinity index and mixed layered phases, and monitoring mineral transitions like smectite to illite, which are often triggered or accelerated by microbial processes in diagenetic environments [3]. Other complementary techniques include transmission electron microscopy (TEM), which visualizes nanoscale microbial imprints and mineral textures [6]; Mössbauer spectroscopy, which determines Fe(II)/Fe(III) ratios [23]; Raman and FTIR spectroscopy, which detect bio-organic compounds associated with clay minerals [15]; and stable isotope analysis, which measures $\delta^{13}C$ and $\delta^{34}S$ anomalies linked to microbial metabolism [25].

2.4.5.3 Significance for early earth and astrobiology

Precambrian clay-rich formations, such as the Doushantuo (China) and Gunflint (Canada), preserve microbial biosignatures including mineralized microfossils, isotopic anomalies, and clay fabric alterations [6, 15]. On Mars, smectite-bearing regions like Mawrth Vallis and Nili Fossae are key astrobiological sites: they formed under aqueous, potentially habitable conditions, can sorb and protect organic matter, and may retain mineralogical evidence of ancient microbial activity [24, 25].

2.4.5.4 Martian rover missions and clay biosignatures

Mars has long been a focus in the search for extraterrestrial life due to geological evidence of past water activity. Clay minerals (phyllosilicates), in particular, are critical because they form in aqueous environments and have high potential to preserve organic molecules and microbial biosignatures. Recent rover missions, especially NASA's Curiosity (Mars Science Laboratory) and ESA's upcoming Rosalind Franklin rover, have targeted clay-rich terrains for this reason.

The Curiosity rover, since its landing in 2012, has explored Gale Crater, a 154 km-wide impact basin that once hosted a lake. X-ray diffraction (XRD) data from the CheMin instrument aboard Curiosity confirmed the presence of smectite clays in the Murray formation and Vera Rubin Ridge, suggesting long-lasting lacustrine conditions [26, 27].

The detection of Fe/Mg-rich smectites, Amorphous silica (a biosignature preserving phase), and organic molecules, such as thiophenes and chlorobenzene [28], suggests that Gale Crater once harbored habitable environments with clay minerals potentially preserving signs of past microbial life.

The Rosalind Franklin rover, part of ESA's ExoMars mission, is scheduled to land at Oxia Planum, a site characterized by extensive exposures of Fe/Mg phyllosilicates, likely formed in neutral to mildly alkaline waters [29]. This landing site hosts layered

clay rich deposits, spectral signatures of nontronite, an Fe rich smectite and geomorphological evidence of ancient surface hydrology, including deltaic formations and inverted channels. Equipped with advanced instruments such as the Mars Organic Molecule Analyzer (MOMA), Raman Laser Spectrometer (RLS), and MicrOmega infrared hyperspectral microscope, the rover will analyze subsurface samples obtained by a 2-meter drill, the deepest ever used on Mars [30]. These instruments will differentiate clay phases in situ, detect preserved biomolecules shielded from surface radiation, and map associations between minerals and organics, which are crucial for authenticating biosignatures [31]. The biosignature preservation potential in Martian clays is supported by their capacity to adsorb and protect organic molecules from degradation [32], their formation in environments potentially analogous to microbial habitats on early Earth [14], and their presence in geologic units dating to the Noachian–Hesperian transition, a period hypothesized to be favorable for life. Together with high-resolution orbital mineralogical data, such as those from CRISM, the ExoMars mission represents a significant step toward identifying ancient biosignatures on Mars.

2.4.5.5 Methodologies for detecting biosignatures in returned Martian samples

The prospect of returning Martian samples to Earth offers a unique opportunity to apply the full suite of advanced analytical techniques to search for biosignatures: molecular, isotopic, or mineralogical evidence of life or biological processes. These analyses can target clay-rich samples, which are prime candidates for biosignature preservation due to their high surface area, cation exchange capacity, and ability to sorb organic matter.

2.4.5.5.1 Mineralogical and structural analysis

Synchrotron-based X-ray diffraction (SXRD) offers ultra-high resolution phase identification and crystallographic analysis, enabling the detection of subtle microbial alterations in clay lattices, such as lattice spacing reductions caused by Fe-reduction. Beyond phase identification, SXRD can reveal micro strain variations and shifts in peak positions that reflect cation exchange or removal during microbial activity, providing insights into reaction mechanisms at the atomic scale. Transmission Electron Microscopy (TEM) provides nanometer-scale imaging of mineral–organic associations, including cell shaped morphologies, lattice defects, and nanocrystalline domains that may represent potential microbial imprints [6]. TEM can also resolve the interface between microbial EPS and mineral surfaces, revealing nucleation sites and alteration fronts. Cryo-TEM and Cryo-SEM techniques preserve the hydrated state of clays and biofilms during imaging, thus avoiding dehydration artifacts and maintaining the integrity of delicate microstructures. These cryogenic methods also allow for the visualization of transient mineral phases and labile organic coatings that would otherwise be lost during conventional preparation, offering a more accurate representation of in situ microbe–mineral interactions.

2.4.5.5.2 Organic molecule detection

Gas Chromatography–Mass Spectrometry (GC–MS) is a powerful technique for detecting and identifying organic compounds such as lipids, thiophenes, and

amino acids that may be of biological origin. By separating complex mixtures and providing mass spectral fingerprints, GC–MS enables both qualitative and quantitative assessments of biomarker distributions. Derivatization agents like TMAH (Tetramethylammonium hydroxide) and MTBSTFA (N-Methyl-N-(tert-butyldimethylsilyl)trifluoroacetamide) are commonly used to extract organics bound to mineral surfaces or trapped within mineral matrices, enhancing detection sensitivity and enabling the analysis of otherwise recalcitrant compounds. These derivatization steps also improve compound volatility and stability, facilitating their analysis via GC–MS without significant thermal degradation. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) offers ultra-high-resolution analysis of complex organic mixtures, resolving thousands of molecular formulas within a single sample. This capability allows for the differentiation of abiotic versus biotic sources based on molecular complexity, heteroatom content, and compound class distributions [28]. When combined, GC–MS and FT-ICR-MS provide a complementary toolkit for reconstructing the diversity, origin, and preservation state of organic molecules associated with microbe–mineral systems, offering critical insights into past and present biosignatures.

2.4.5.5.3 Isotopic analysis

Stable Isotope Ratio Mass Spectrometry (IRMS) measures isotopic compositions such as $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ with high precision, often capturing characteristic biological fractionation patterns. Light $\delta^{13}C$ signatures in carbonates or organic matter, for instance, can indicate carbon fixation pathways driven by microbial activity. Similarly, $\delta^{15}N$ and $\delta^{34}S$ variations can reveal nitrogen and sulfur cycling processes, respectively, that are frequently mediated by microbial metabolisms. Secondary Ion Mass Spectrometry (NanoSIMS) extends these capabilities by providing micron- to submicron-scale spatial resolution of isotopic distributions across mineral–organic interfaces. This enables the direct association of isotopic anomalies with specific microstructures, such as microbial cell outlines or EPS-rich regions, effectively linking geochemical signals to morphological biosignatures. When used together, IRMS and NanoSIMS provide a powerful combination for both bulk and spatially resolved isotopic characterization, allowing researchers to identify, localize, and interpret biosignatures with a high degree of confidence.

2.4.5.5.4 Spectroscopy techniques

Raman Spectroscopy identifies carbonaceous matter, mineral phases, and potential biological pigments or structural biomolecules. Its ability to detect the degree of structural order in carbon, particularly through the analysis of the D/G band ratio, can provide strong evidence for biogenic carbon when combined with morphological context. This non-destructive technique is especially valuable for studying delicate microfossils or mineral-organic associations in situ. X-ray Absorption Near-Edge Spectroscopy (XANES) determines the oxidation states and coordination environments of elements such as iron, sulfur, and carbon, offering detailed insights into past microbial metabolisms and redox-sensitive changes associated with biological activity. When applied to microbe–mineral systems, XANES can reveal subtle chemical fingerprints of biotic interactions, complementing morphological and isotopic data to strengthen biosignature interpretations.

2.4.5.5.5 Microscopy and imaging

Focused Ion Beam (FIB)–Scanning Electron Microscopy (SEM) enables the precise slicing of clay aggregates and microfossils at the nanometer scale, facilitating the preparation of site-specific thin sections for detailed isotopic or spectroscopic analysis. This technique allows researchers to target specific regions of interest identified through preliminary imaging, ensuring that subsequent analyses focus on features with the highest potential for biosignature preservation. Three-dimensional tomography techniques, such as ptychographic X-ray computed tomography, enable the non-destructive reconstruction of organic mineral structures without physical sectioning. This preserves delicate and fragile features that might otherwise be lost or altered during sample preparation, providing unprecedented insight into the spatial arrangement and connectivity of biosignature bearing phases.

2.4.5.5.6 Biomolecule detection

Proteomics and genomics (including metagenomics) approaches can be applied when preserved DNA, RNA, or peptides are present within the sample. Techniques such as next-generation sequencing (NGS) and peptide mass fingerprinting can help identify microbial lineages, metabolic pathways, and functional traits linked to past or present biosignatures. Given the extremely low biomass often encountered in ancient or extraterrestrial samples, contamination control is crucial at every stage, from sample acquisition to laboratory processing, to ensure authenticity of the detected biomolecules [33]. These methods, when integrated with mineralogical, isotopic, and organic geochemical analyses, can provide a comprehensive understanding of the biological and environmental context of the studied systems.

Returned Martian samples will be analyzed in biosafety level containment laboratories with Earth based sterilization controls and blanks. Instrument protocols will be validated against Mars analog materials (e.g., Atacama clays, hydrothermal sediments) to distinguish Martian signals from terrestrial contaminants.

2.4.5.5.7 Limitations and complementary methods

X-ray diffraction (XRD) has certain limitations: it cannot detect amorphous or poorly crystalline materials, and mixed-layer clays often require complex modeling and profile fitting to interpret their diffraction patterns accurately [3]. Therefore, XRD analyses should be complemented with techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), or Transmission Electron Microscopy (TEM) to obtain detailed information on morphology and elemental composition [17].

Advances in spectroscopic tools like Raman and infrared techniques have augmented the study of clay minerals, enabling precise detection of both crystalline and amorphous phases. Raman spectroscopy, for instance, facilitates the identification of vibrational modes unique to specific clays, while infrared spectroscopy provides insights into hydroxyl bonding and the presence of organic residues. These methods complement XRD and can verify ambiguous findings, particularly in samples with complex mineralogical compositions. In planetary exploration, these methods are invaluable for probing extraterrestrial soils, such as Martian regolith, where mixed signals from minerals and potential organics demand nuanced interpretation.

3. Engineering perspectives in clay mineral identification using X-ray diffraction (XRD)

Engineering applications of X-ray diffraction (XRD) extend beyond mineralogical classification to the practical evaluation and design of infrastructure in environments containing clay-rich soils. The mineralogical composition identified through XRD directly influences engineering properties such as strength, compressibility, swelling potential, and permeability. These characteristics govern the performance of pavements, foundations, retaining structures, earthworks, and containment systems.

This section presents the integration of XRD results into engineering analyses, focusing on their role in expansive soil characterization, prediction of soil–water characteristic behavior, calibration of mechanistic–empirical design models, and evaluation of stabilization treatments. It also addresses the use of XRD in environmental containment, offshore geotechnics, and the long-term monitoring of mineralogical stability in engineered systems. The discussion emphasizes how mineralogical precision obtained from XRD enhances the accuracy, reliability, and durability of engineering designs.

3.1 XRD in expansive soil characterization

Expansive soils, particularly those dominated by smectite-group minerals such as montmorillonite, exhibit significant volumetric changes in response to moisture fluctuations. These changes can cause severe distress in pavements, shallow foundations, retaining structures, and slopes [34, 35]. X-ray diffraction (XRD) provides the most reliable means of identifying these swelling-prone minerals by detecting their diagnostic basal spacings, which expand from ~12–15 Å (air-dried) to ~17 Å after ethylene glycol treatment [2].

The direct quantification of expansive mineral content enables engineers to predict heave potential more accurately than index tests such as Atterberg limits, which may underestimate swelling risk when plasticity index values are moderate but smectite content is high [36]. For example, in the Dallas–Fort Worth region, XRD confirmed montmorillonite dominance in subgrades linked to differential heave in residential foundations [35]. This mineralogical insight allows for the selection of mitigation strategies, including moisture barriers, soil replacement, or lime stabilization. These strategies should be implemented only after confirming mineral compatibility to avoid deleterious reactions such as sulfate-induced heave [37]. **Table 1** summarizes the engineering implications of major clay minerals, including their typical basal spacings, cation exchange capacities (CEC), swelling potentials, and common engineering concerns, as compiled from mineralogical and geotechnical sources [2, 38, 39].

Mineral	Typical basal spacing (Å)	CEC (meq/100 g)	Swelling potential	Common engineering concerns
Smectite/ Montmorillonite	12–15 (air-dried), 17 (glycolated)	80–150	Very high	Pavement heave, foundation movement, slope instability
Illite	10	10–40	Low–moderate	Moderate shrink–swell, frost susceptibility
Kaolinite	7	3–15	Very low	Low plasticity, good stability in construction

Table 1.
Engineering implications of major clay minerals.

3.2 Integration of XRD with soil–water characteristic curves (SWCC) and suction models

The shape and position of the Soil–Water Characteristic Curve (SWCC) are strongly influenced by clay mineralogy. Smectite-rich soils typically exhibit higher air-entry values, prolonged moisture retention, and greater hysteresis between drying and wetting cycles than kaolinitic soils [40, 41]. These characteristics directly impact shear strength, volume change, and resilient modulus in unsaturated soil mechanics [39, 42].

In engineering practice, XRD-derived mineral profiles are integrated into SWCC fitting models to improve parameter estimation and reduce model error. This approach has proven essential in mechanistic–empirical pavement design, where suction–moisture–deformation relationships govern subgrade performance [40, 43, 44]. By calibrating SWCCs with mineralogy-verified suction behavior, designers can better predict seasonal deformation, edge lift, and center lift in expansive soil environments. **Figure 2**. Soil–Water Characteristic Curves (SWCC) illustrating the influence of clay mineralogy on unsaturated soil behavior. Data and conceptual model (adapted from Sahin [40]).

3.3 Soil stabilization design and risk assessment

Chemical stabilization, commonly performed using lime or cement, is a widely used method for improving the engineering properties of clay soils. However, the effectiveness and long-term durability of stabilization depend heavily on the initial mineralogical composition.

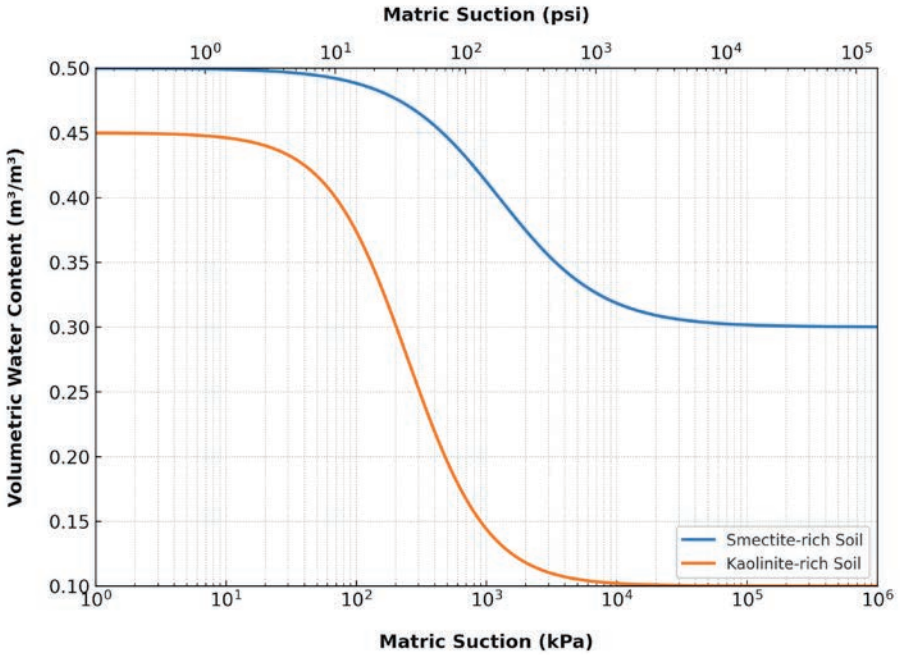

Figure 2.
Soil–Water Characteristic Curves (SWCC) illustrating the influence of clay mineralogy on unsaturated soil behavior. Data and conceptual model.

Smectite-rich soils often respond well to lime treatment, forming stable calcium silicate hydrates (CSH). In contrast, soils containing appreciable sulfates may generate expansive ettringite, which can lead to post-construction heave [37].

XRD plays a crucial role in stabilization design by identifying both reactive clay minerals and deleterious phases such as gypsum before treatment [45]. After treatment, XRD can confirm the formation of target hydration products and determine whether expansive minerals remain, enabling performance-based quality assurance. This mineralogical verification is critical for avoiding premature failures and for ensuring that the stabilization method aligns with site-specific geochemical conditions.

3.4 Cation exchange capacity (CEC) and environmental engineering applications

Clay minerals exhibit a wide range of Cation Exchange Capacity (CEC) values, with smectites and vermiculites typically possessing significantly higher CECs than kaolinites [38]. High-CEC clays are capable of retaining nutrients, heavy metals, and organic contaminants, making them highly effective in environmental containment systems such as landfill liners, mine tailings covers, and contaminant barriers.

XRD supports environmental engineering by confirming the mineral phases responsible for high CEC and by monitoring changes in mineralogy that could reduce contaminant retention over time. For example, in geosynthetic clay liners used for waste management, XRD verification of bentonite purity is essential to ensure long-term containment performance. Additionally, XRD can detect mineralogical transformations such as the degradation of smectite, which may compromise barrier integrity under chemical, thermal, or mechanical stress.

3.5 Offshore and subsea geotechnical applications

In offshore engineering, XRD is widely applied to characterize seabed sediments beneath subsea structures, mudmats, and pipelines [46]. Identifying clay minerals prone to strain softening, such as certain smectites, is essential for assessing cyclic degradation under wave and current loading.

For suction caisson and pile foundations, mineralogy determined by XRD helps predict consolidation rates, creep behavior, and cyclic strength degradation, resulting in more accurate load–displacement modeling. In subsea pipeline design, knowledge of the clay mineral composition supports the assessment of upheaval buckling risks and potential changes in embedment resistance throughout the service life. Such mineralogical insights are particularly valuable for high-consequence offshore assets where maintenance access is limited.

3.6 Foundation and structural interaction Modeling

Expansive clay mineralogy significantly influences both vertical and lateral pressures acting on foundations and retaining structures. In high-plasticity clays, lateral swelling pressures can reach 10 to 20 times the active earth pressures estimated using classical earth pressure theories [47].

Finite element models that incorporate XRD-verified mineralogical data, as demonstrated in Bulut's [48] slab-on-grade analyses, simulate moisture-induced stress changes and edge uplift more realistically than models that rely solely on index

properties [48]. This mineralogy-based modeling approach enhances the reliability of designs for drilled shafts, retaining walls, and slabs-on-grade in expansive soil environments.

3.7 Laboratory protocols and best practices for engineering use of XRD

Reliable mineral identification depends on rigorous sample preparation and analysis. Best practices include isolating the <2 μm clay fraction, preparing oriented mounts, and applying sequential treatments such as air drying, ethylene glycolation, and heating to distinguish smectite, kaolinite, and illite [49].

For engineering applications, XRD results should be cross-validated with complementary techniques such as Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM–EDS) to obtain morphological and compositional data, or Differential Thermal Analysis (DTA) to assess thermal stability. This integrated, multi-method approach ensures that mineralogical data are robust and suitable for direct incorporation into geotechnical design and modeling.

3.8 Durability and Long-term performance monitoring of clay-rich soils

The long-term engineering performance of clay-rich soils depends not only on their initial mineralogy but also on how that mineralogy evolves after construction. Environmental factors such as wet–dry cycling, freeze–thaw action, chemical leaching, and biological activity can trigger transformations such as the smectite-to-illite reaction, which can reduce swelling potential but may also lead to strength loss [3, 17].

XRD enables the detection of gradual changes in mineral assemblages during the service life of a structure. In transportation engineering, periodic XRD testing of subgrades has been used to identify lime carbonation and the loss of cementitious phases, which correlate directly with reductions in modulus and increased rutting risk [37]. Similarly, in earth dam cores, XRD monitoring has detected the dissolution of expansive phases under alkaline seepage conditions, allowing preventive maintenance before deformation becomes critical [50].

3.9 Integration of XRD with remote sensing and GIS for large-scale mapping

Hyperspectral remote sensing enables regional mapping of clay mineral distributions through spectral absorption features near 2.2 μm. However, spectral data alone cannot always distinguish similar phyllosilicates (e.g., kaolinite vs. halloysite) without ground validation. XRD provides the definitive mineralogical confirmation for remote sensing classifications, enhancing the accuracy of geotechnical hazard maps [51, 52].

In practice, this integration is invaluable for early-stage project planning. For example, pipeline route selection in Australia has used hyperspectral imagery combined with GIS, then verified with targeted XRD sampling to avoid swelling clay zones [53]. Transportation agencies have similarly combined airborne mineral maps with XRD-verified ground surveys to tailor pavement designs for moisture-susceptible subgrades.

3.10 XRD in heritage conservation and archaeological geotechnics

XRD also plays a role in the preservation of heritage structures built with earthen materials such as adobe, cob, and ancient mortars. These materials depend on specific

clay mineral assemblages for cohesion and durability, which can be altered over centuries due to weathering or incompatible restoration methods [54].

In archaeological geotechnics, XRD is used to match repair materials to the original mineralogical profile, ensuring chemical compatibility and avoiding deleterious reactions. For instance, in restoring the Great Mosque of Djenné, Mali, XRD confirmed that local kaolinite-rich clays were the primary binder, guiding the selection of restoration soils to maintain structural stability under seasonal wetting–drying cycles [55]. This application demonstrates the cross-disciplinary importance of engineering mineralogy in both modern infrastructure and cultural heritage preservation.

4. Summary

X-ray diffraction (XRD) provides a direct and reliable means of identifying clay minerals, offering valuable insights that extend beyond laboratory analysis into practical engineering applications. Its precise mineralogical characterization supports geological and geochemical investigations while directly informing geotechnical design, performance prediction, and long-term maintenance strategies.

By integrating XRD data into engineering models, practitioners can better anticipate soil behavior, optimize stabilization measures, and improve the durability of infrastructure founded in clay-rich environments. The continued development of XRD techniques, coupled with complementary analytical methods, will further enhance its role in addressing complex geotechnical and environmental challenges. As a result, XRD remains a critical bridge between fundamental mineral science and engineering practice, contributing to more resilient and sustainable infrastructure systems.

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