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Identification of Clay Minerals by using Different Methods

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Abstract

Soil structure depends on clay and its minerals. The soils with lesser quantity of clay content have a simple structure, whereas soils with more quantity of clay content have complex structures and more pore size pattern. Their response to changes in water content is structurally quite different from that of sandy soils. Clays have a wider specific surface, often predominantly negatively charged, that retains nutrients against leaching and reacts with hydrogen and aluminium ions, while buffering the soil against extreme level of pH changes. The clay itself may be a source of plant nutrients when it degrades. Clay minerals, through their physical and chemical properties, affect soil fertility by controlling nutrient supplies and availability, through the sequestration and stabilization of soil organic matter, by controlling soil physical properties through micro-aggregate formation, by influencing soil acidity and controlling.

Introduction

The clay minerals are a group of minerals that occur as colloidal crystals in clay. They are all hydrated aluminosilicates having layered crystal structures. They may contain significant amounts of iron, alkali metals, or alkaline earths. The clay minerals are very much importance in the soil texture and to maintain the health of the soil system (Van Olphen and Fripiat, 1979). The clay minerals were identified by different methods to know the application and its potential role. The clay minerals were identified by using X-ray Powder Diffraction (XRD), Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM).

X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

Principle

To observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization & wavelength or energy-absorption, scattering or fluorescence of the X-rays may occur. The diffraction pattern serves as a fingerprint of each mineral is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic

radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$).

Bragg's Law

- This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.

- Bragg's law, this relationship may be expressed as,

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

Where,

n = integral numbers,

λ = wavelength (\AA),

d = interplaner or lattice spacing, &

θ = angle of incidence beam or angle of diffraction.

- Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation.

Applications, Strengths and Limitations of XRD

- X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g., minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. Characterization of crystalline materials. Identification of fine grained minerals such as clays and mixed layer clays that are difficult to determine optically.

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral. In most cases, it provides an unambiguous mineral determination. Minimal sample preparation is required. XRD units are widely available. Data interpretation is relatively straight forward.

- Homogeneous and single phase material is best for identification of an unknown. Must have access to a standard reference file of inorganic compounds. Requires tenths of a gram of material which must be ground into a powder. For mixed materials, detection limit is ~ 2% of sample. For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated.

Transmission Electron Microscope (TEM)

Principle

Beam of electron is transmitted through an ultra thin specimen, interacting with the specimen. The image is magnified and focused on fluorescent screen, on to a layer of photographic film or to be detected by a sensor such as CCD camera. TEM are capable of imaging at higher resolution than light microscope and even atoms can be identified.

Components of TEM includes Vacuum system, Specimen stage, Electron gun, Electron lens and Apertures and the three stages of lensing in TEM includes Condenser lens (for primary beam formation), Objective lens (focus the beam down onto the sample) & Projector lens (Expand the beam onto the phosphor screen). The magnification of the TEM is due to the ratio of the distances between the specimen and objective lens.

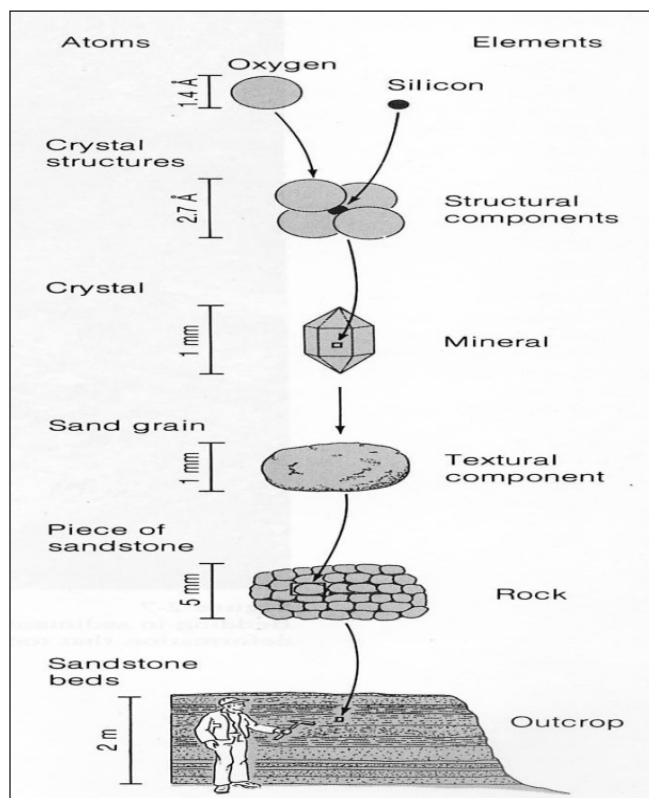


Figure 1: Transmission electron microscopic (TEM) studies on clay minerals from sandstones

Transmission electron microscopic (TEM) studies of clay minerals from sandstones have employed conventional 100 kV instruments, and most have been made with clay extracts. Two methods of identification are available on transmission electron microscopes; these are, selected area electron diffraction (SAD) and X-ray analysis. The clay minerals (i.e., kaolin-group minerals, smectites, micas, and chlorites) can be readily identified by SAD techniques by their basal spacings.

The tilting stages on most TEM instruments allow particles to be rotated into a position for the basal planes to diffract. This can be detected in micrographs as the grains appear at their darkest. The bulk chemistry of a mineral can be determined by analysis of X-rays (XRA) emitted as a result of electron irradiation of the sample. This technique is less precise for mineral identification than SAD; however, it can assist in the identification of clay minerals which have similar d-spacings, e.g., different types of chlorites, smectites, etc. Mineral phases can also be differentiated by comparing “finger print” elemental analyses (Lazarev, 1974).

Effect of Increasing Voltage on Transparent Area

Conventional TEM instruments operate at 100 kV, or occasionally at 200 kV, and the area transparent to the electron beam at this voltage is substantially less than that at 1000 kV. The effect of increasing the accelerating voltage on the area of foil transparent to the beam. At 100 and 200 kV little detail of the kaolinite grain can be seen; whereas, at 1000 kV the fine structure and the smaller particles at the grain edge become apparent. At 1000 kV it is also possible to relate features seen in the electron microscope. With 100 kV instruments such a comparison is impossible, and the spatial relationships between clays and other minerals are difficult to resolve even at 200 kV. The problem is mainly due to the fact that the clays etch much more slowly than does the quartz and araldite cement. Consequently, in very thin areas, such as those needed for 100 and 200 kV TEM studies, the quartz etches out, and the quartz-rich areas of the foils tend to fall apart. The most important pieces of information required to characterize a mineral are: Crystal structure and Chemical composition.

TEM is capable to obtain both structure and chemical information from a small area down to 1 nm (in diameter). No other technique can provide imaging (both texture/ fabric and internal structure), crystallographic information (electron diffraction), and chemical composition simultaneously from a very small region (1 nm). TEM is a logical complement and extension of some of the more established mineralogical techniques and instruments.

Application and Limitation of TEM

- Minerals identification are mainly defect and microstructure; HRTEM – Determination of the atomic structure, perfect and defected minerals/ crystals.
- To give a general overview/ review of the application of TEM in the mineralogical and geological sciences research. To show examples of mineralogical and geological researches that has been utilizing TEM. To stimulate, hopefully, the direction of future mineralogical and geological research in the application of TEM.
- Poor vacuum in the TEM can cause several problems. Deposition of gas inside the TEM over the specimen also

can cause damage. Extensive sample preparation. Time consuming.

Scanning Electron Microscope (SEM)

SEM follows the De Broglie’s wave equation.

- This wave equation relates the velocity of the electrons to its wavelength.

$$\lambda = h / mv$$

Where,

λ = wavelength,

h = plank’s constant,

m = rest mass of electron,

v = velocity.

- An electron of charge and mass when passing through a potential difference of volts (joules coulomb⁻¹) acquires a kinetic energy. Velocity of electrons will reach the speed of light in vacuum.

Principle

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons, diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence-CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e., for rapid phase discrimination).

X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is “excited” by the electron beam. SEM analysis is considered to be “non-destructive”; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

Components of SEM

Essential components of all SEMs including the followings namely, Electron Source (“Gun”), Electron Lenses, Sample Stage, Detectors for all signals of interest, Display/ Data output devices. Infrastructure Requirements

for SEM is Power Supply, Vacuum System, Cooling system, Vibration-free floor, Room free of ambient magnetic and electric fields.

Working of SEM

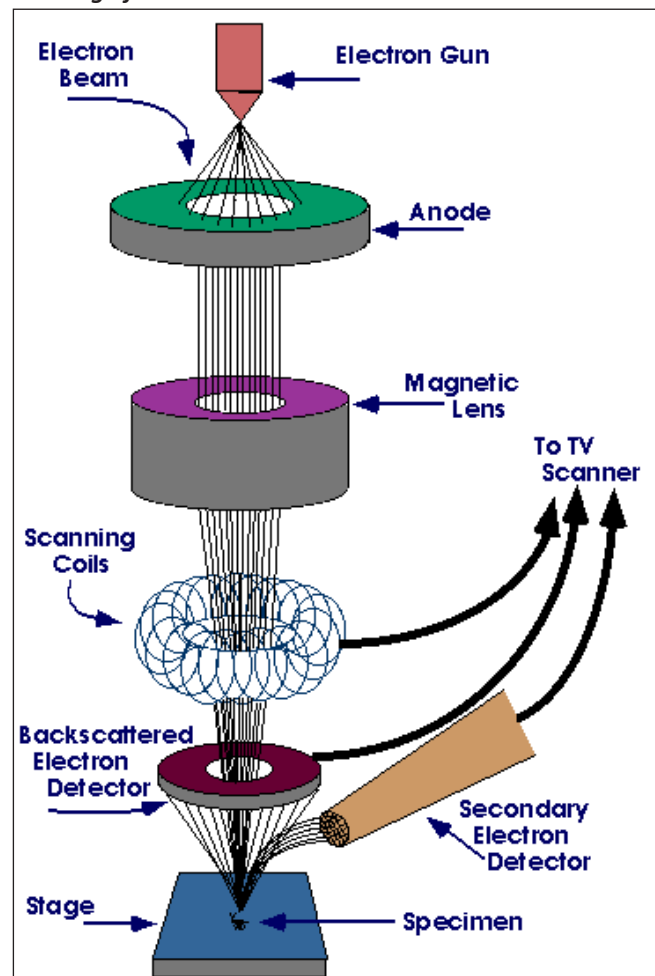


Figure 2: A view of Scanning Electron Microscope

A SEM functions in a similar way to a traditional light microscope. An electron gun generates electrons, which are then accelerated by an electric potential. There are then condensing lens that collimate the electrons into small beam. While lenses in an optical system are made of curved pieces of plastic or glass, in a SEM a lens is made by a coil of current-carrying wire. This coil makes a magnetic field which exerts a force on the moving electrons. After the condensing lens is another coil which scans the beam of electrons over the sample. There is a final objective lens that focuses the beam to a small spot on the sample. The electron beam hits the sample and causes secondary electrons to leave the sample.

The secondary electrons hit a detector which generates an electrical signal. This electrical signal is processed by a computer into an image. All the SEM components are contained inside a vacuum chamber to minimize electron-gas

interactions. SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

Applications, Strengths and Limitations of SEM

The SEM is routinely used to generate high-resolution images of shapes of objects and to show spatial variations in chemical compositions (acquiring elemental maps, discrimination of phases and compositional maps). The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Backscattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors (EBSD) can be used to examine microfabric and crystallographic orientation in many materials. The image quality was affected by lens, spherical and chromatic aberrations.

There is arguably no other instrument with the breadth of applications in the study of solid materials that compares with the SEM. The SEM is critical in all fields that require characterization of solid materials. While this contribution is most concerned with geological applications, it is important to note that these applications are a very small subset of the scientific and industrial applications that exist for this instrumentation. Most SEM's are comparatively easy to operate, with user-friendly "intuitive" interfaces. Many applications require minimal sample preparation. For many applications, data acquisition is rapid. Modern SEMs generate data in digital formats, which are highly portable.

Samples must be solid and they must fit into the microscope chamber. Maximum size in horizontal dimensions is usually on the order of 10 cm; vertical dimensions are generally much more limited and rarely exceed 40 mm. For most instruments samples must be stable in a vacuum on the order of 10^{-5} - 10^{-6} torr. Samples likely to outgas at low pressures (rocks saturated with hydrocarbons, "wet" samples such as coal, organic materials or swelling clays, and samples likely to decrepitate at low pressure) are unsuitable for examination in conventional SEM.

Differential Thermal Analysis (DTA) and Its Applications

Differential thermal analysis (DTA) consists of simultaneously heating a test sample and a thermally inert substance at constant rate (usually about $10\text{ }^{\circ}\text{C min}^{-1}$) to over $1000\text{ }^{\circ}\text{C}$ and continuously measuring differences in temperature and the inert material DT. Endothermic (take up heat) or exothermic (liberate heat) reactions can take place at different heating temperatures. The mineral types can be characterized based on those signatures. A DTA

curve can be used only as a finger-print for identification purposes but usually the applications of this method are the determination of phase diagrams, heat change measurements and decomposition in various atmospheres. The clay minerals variations were identified by sedimentation; mainly mineralogy correlates with particle size. Segregation by size forming layers of different color, mineralogy and varying layers.

Conclusion

To identify the clay minerals in soil ecosystem by using different methods namely Differential Thermal Analysis, Scanning Electron Microscope (SEM), Transmission Electron Microscopic (TEM) *etc.*, were employed to know the variations in clay minerals and its composition to improve the soil texture. The prime most importance for the identification

of clay minerals are to know water holding capacity, structure and chemical composition of clay minerals and its classification, characteristics, cation exchange capacity, swelling capacity, surface charge properties, adsorptive properties, plasticity and dispersion or flocculation *etc.*

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