



NIGERIA MARITIME UNIVERSITY

Okerenkoko, Warri South-West, Delta State

Department of Marine Geology

MGY 421

Advanced Mineralogy

Lecture Note

*Analytical Methods in Mineralogy
Clay Minerals and Marine Authigenic Minerals
Ore Mineralogy*

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Course information

This note covers three parts of MGY 421. The first describes the instrumental methods used to identify minerals and measure their composition: X-ray diffraction, scanning electron microscopy, electron microprobe analysis and X-ray fluorescence. The second deals with the clay minerals and the minerals that form in marine sediments. The third introduces ore mineralogy: the study of opaque ore minerals in reflected light, their textures and their use in exploration and mineral processing. The other topics of the course are covered in the other part of the course.

Item	Detail
Course	MGY 421: Advanced Mineralogy
Level	400 level, first semester, 2026/2027 session
Department	Marine Geology
Institution	Nigeria Maritime University, Okerenkoko, Warri South-West, Delta State
Lecturer	Dr. Daniel Tuoyo Amiwero
Part covered by this note	Analytical methods; clay and marine authigenic minerals; ore mineralogy

Learning outcomes

At the end of this part of the course, you should be able to:

1. Explain how X-rays are produced and how they interact with crystals, and use Bragg's law to relate diffraction angles to the spacing of lattice planes.
2. Describe how a powder X-ray diffraction pattern is obtained and used to identify minerals, estimate their proportions and crystallite size.
3. Explain the interactions of an electron beam with a sample, and the principles and uses of the SEM, EDS, WDS and the electron microprobe.
4. Calculate a mineral formula from an electron microprobe analysis, and choose a suitable analytical method for a given problem.
5. Describe the structures, classification, properties and identification of the clay minerals.
6. Explain the origin and significance of clay minerals and authigenic minerals such as glauconite, phosphorite, zeolites and evaporites in marine sediments.
7. Identify common ore minerals in reflected light using their colour, reflectance, anisotropy, internal reflections and hardness.
8. Interpret ore textures and paragenesis, and calculate modal mineralogy and metal grade from point counts.

Why this matters to a marine geologist

Most marine sediments are made of fine-grained minerals that cannot be identified with a hand lens or an ordinary microscope. Clays, glauconite, phosphorite, zeolites and fine sulphides record the climate, the sources of sediment and the chemistry of the water in which they formed. They also control the engineering behaviour of seabed soils and the quality of reservoirs and seals in the Niger Delta. X-ray diffraction and electron beam methods are the everyday tools for studying them. Ore mineralogy, in turn, links the study of mineral deposits,

such as seafloor sulphides and heavy mineral sands, to their exploration and processing. Together, these methods allow the marine geologist to turn a sample of mud, sand or ore into reliable data.

Section 1: Analytical methods in mineralogy

1.1 Why instrumental methods are needed

The hand lens and the polarising microscope remain the first tools of the mineralogist, but they have limits. Many minerals are too fine-grained to be seen, as in clays, cements and marine muds; many are opaque; and minerals with similar appearance can differ greatly in composition. Instrumental methods answer three questions that optical methods cannot fully answer:

- **What is the crystal structure?** This identifies the mineral, and is answered mainly by **X-ray diffraction** (XRD).
- **What is the chemical composition, and how does it vary from grain to grain?** This is answered by **electron beam methods**: the scanning electron microscope (SEM) with energy-dispersive spectrometry (EDS), and the electron probe microanalyser (EPMA) with wavelength-dispersive spectrometry (WDS).
- **What is the bulk composition of the rock or sediment?** This is answered by **X-ray fluorescence** (XRF) and by solution methods such as inductively coupled plasma (ICP) spectrometry.

Method	What it measures	Typical sample	Spatial resolution	Typical detection limit
Powder XRD	Crystal structure; mineral identity and proportions	Powder, a few grams or less	Bulk	About 1–2 wt% of a mineral
SEM-EDS	Images; element composition of grains	Polished section or grains, coated	About 1 µm	About 0.1 wt% of an element
EPMA-WDS	Accurate element composition of grains	Polished section, coated	About 1–2 µm	About 0.01 wt% (100 ppm)
XRF	Bulk major and trace element chemistry	Fused bead or pressed powder	Bulk	Major elements to 0.01 wt%; traces to a few ppm
ICP-MS, LA-ICP-MS	Trace elements and isotopes	Solution, or laser spot on a section	Bulk, or 10–100 µm	ppb to sub-ppm

All of these methods rely on the interaction of radiation or particles with matter, and most of them use **X-rays**. We begin with how X-rays are produced.

1.2 X-rays and their production

X-rays are electromagnetic radiation with wavelengths of about 0.01 to 10 nm, similar to the distances between atoms in crystals (0.1 to 0.5 nm). Wavelength λ and photon energy E are related by

$$E = \frac{hc}{\lambda} \quad E \text{ (keV)} \approx \frac{12.398}{\lambda \text{ (Å)}}$$

In an **X-ray tube**, electrons are accelerated by a voltage of 30 to 60 kV and strike a metal target, the anode, commonly of copper (Cu), cobalt (Co) or molybdenum (Mo). Two kinds of X-rays are produced (Figure 1.1):

- **Continuous radiation** (*Bremsstrahlung*, “braking radiation”) is produced as the electrons are slowed down by the atoms of the target. It forms a smooth spectrum whose shortest wavelength corresponds to the full energy of the electrons.
- **Characteristic radiation** is produced when an incoming electron knocks out an electron from an inner shell (the K shell) of a target atom. An electron from an outer shell falls into the vacancy and the difference in energy is emitted as an X-ray of a precise wavelength. A transition from the L shell to the K shell gives the **K α** line, and from the M shell the weaker **K β** line.

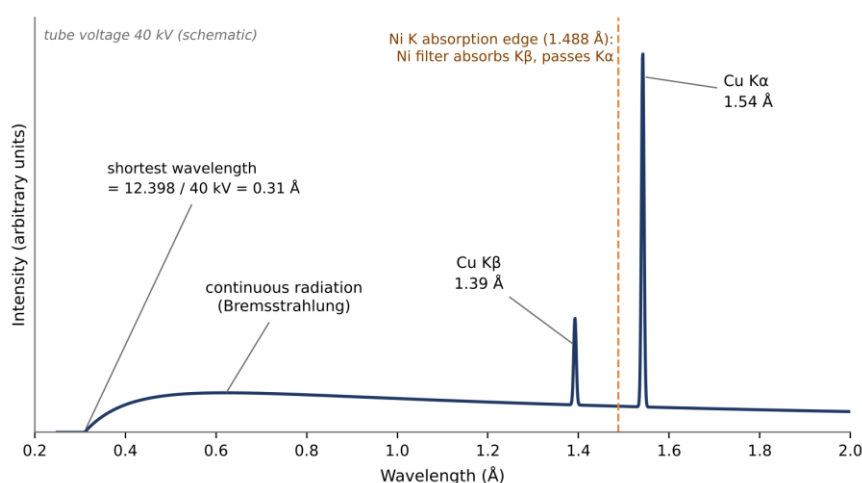


Figure 1.1. Spectrum of a copper X-ray tube (schematic): the smooth continuous radiation and the sharp characteristic K α and K β lines. A nickel filter removes most of the K β line, leaving nearly monochromatic Cu K α radiation for diffraction.

For diffraction, the Cu K α line, with a wavelength of 1.5406 Å (K α_1), is used almost universally, and a nickel filter or a monochromator removes the K β line. The characteristic lines have energies that depend on the atomic number Z of the element emitting them. **Moseley's law** states that

$$\sqrt{\nu} = k (Z - \sigma)$$

where ν is the frequency of the line and $\sigma \approx 1$ for K α lines. In energy terms, $E_{K\alpha} \approx 10.2 \text{ eV} \times (Z - 1)^2$. For copper ($Z = 29$) this gives about 8.0 keV, close to the measured 8.05 keV. Because every element has its own characteristic lines, measuring them identifies the elements present: this is the basis of EDS, WDS and XRF.

1.3 X-ray diffraction

Bragg's law. A crystal consists of atoms arranged in a regular lattice, which can be described as sets of parallel planes with spacing d . When a beam of X-rays strikes the crystal, each plane reflects a small part of it. The reflected waves reinforce one another only when the extra path travelled by the wave reflected from the deeper plane, $2d\sin\theta$, is a whole number of wavelengths (Figure 1.2):

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

where θ is the angle between the beam and the planes and n is the order of reflection. In practice n is set to 1 and higher orders are treated as reflections from planes with smaller spacing. Each set of planes is labelled by its **Miller indices** (hkl).

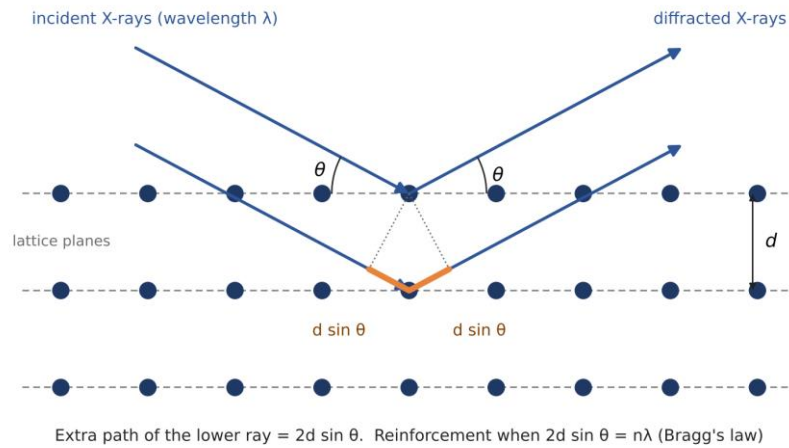


Figure 1.2. Bragg's law: X-rays reflected from successive lattice planes are in phase, and reinforce one another, only when the extra path length $2d \sin \theta$ equals a whole number of wavelengths.

Spacing of planes and unit cell. The spacing d_{hkl} depends on the dimensions of the unit cell. For the cubic, tetragonal and hexagonal systems:

$$\text{Cubic: } \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

$$\text{Tetragonal: } \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

$$\text{Hexagonal: } \frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$

Worked example: identifying a mineral from a peak. A strong peak is recorded at $2\theta = 26.64^\circ$ using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Then $\theta = 13.32^\circ$ and

$$d = \frac{\lambda}{2\sin\theta} = \frac{1.5406}{2 \times \sin 13.32^\circ} = \frac{1.5406}{0.4608} = 3.343 \text{ \AA}$$

This is the strongest reflection, (101), of quartz. In a second sample, the strongest peak of a cubic mineral is at $2\theta = 31.69^\circ$, giving $d = 2.821 \text{ \AA}$. If this is the (200) reflection, then $a = d\sqrt{h^2 + k^2 + l^2} = 2.821 \times 2 = 5.64 \text{ \AA}$, the unit cell of halite (NaCl).

The powder diffractometer. In mineralogy, XRD is usually carried out on a fine powder (less than about $10 \mu\text{m}$), in which millions of tiny crystals lie in all orientations, so that every set of planes is represented. In the common **Bragg-Brentano** diffractometer, the X-ray tube and the detector move around the flat powder sample so that the angle of incidence and the angle of reflection are always equal. The detector records the intensity of diffracted X-rays against the angle 2θ , producing a **diffraction pattern** (Figure 1.3). Patterns are typically recorded from about 3° to $70^\circ 2\theta$.

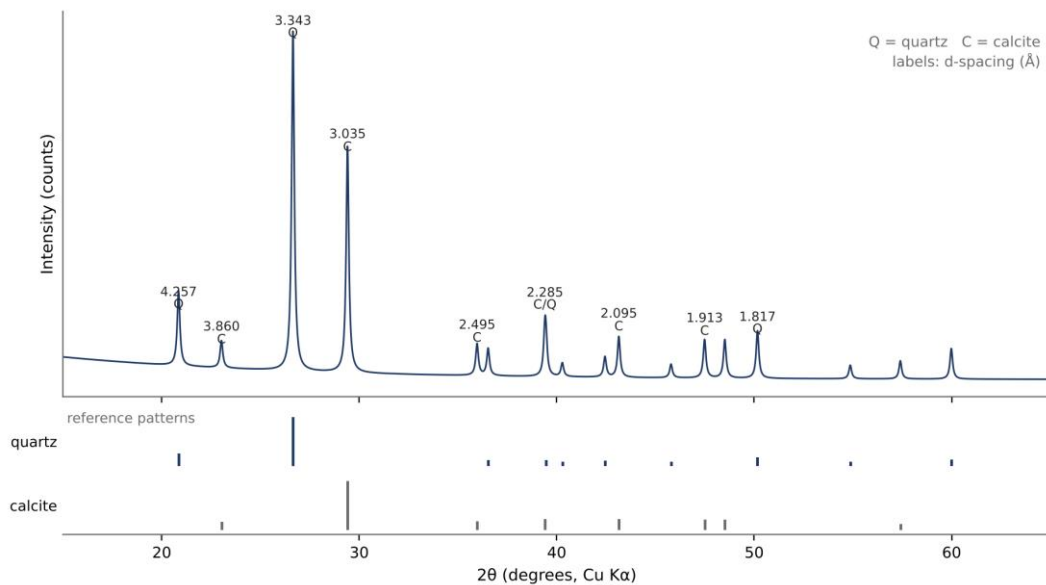


Figure 1.3. A simplified powder diffraction pattern (Cu K α) of a sand containing quartz and calcite. Each peak is labelled with its d-spacing; the strongest peaks of each mineral identify it.

Reading a pattern. Three properties of the peaks carry information:

1. **Positions** (2θ , converted to d) depend on the size and shape of the unit cell. They identify the mineral, and small shifts reveal changes in composition, such as the substitution of Mg for Fe in a solid solution or of Mg in calcite.
2. **Relative intensities** depend on the kinds and positions of atoms in the cell, and on the amount of each mineral present.
3. **Widths** depend on the crystallite size and on strain in the crystals.

Identification. Each mineral has a characteristic set of d-spacings and intensities. The measured pattern is compared, usually by computer search-match, with reference patterns in databases such as the Powder Diffraction File of the International Centre for Diffraction Data (ICDD). A mixture gives the sum of the patterns of its minerals, and the three or four strongest peaks of each are usually enough to identify it.

Quantitative analysis. The proportions of minerals in a mixture can be estimated from the intensities of their peaks, by comparison with an internal standard (such as corundum) or by the **Rietveld method**, which fits the whole calculated pattern to the measured one by refining the structure and amount of each mineral. Accuracies of a few weight per cent are typical. Minerals present at less than about 1–2 wt%, and amorphous materials such as volcanic glass and opal, are hard to detect.

Crystallite size. Very small crystals give broadened peaks. The **Scherrer equation** estimates the mean crystallite size τ :

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where β is the broadening of the peak (its full width at half maximum, in radians, after subtracting the instrumental width) and $K \approx 0.9$. For example, a quartz peak at $2\theta = 26.64^\circ$ broadened by 0.25° ($\beta = 0.00436$ rad) gives $\tau = 0.9 \times 1.5406 / (0.00436 \times \cos 13.32^\circ) \approx 327 \text{ \AA}$, or about 33 nm. The method is useful for crystallites smaller than about 100 nm, such as clays.

Sample preparation. Good results depend on preparation: grinding to a fine, uniform powder (often in a micronising mill), avoiding preferred orientation of platy minerals for random

powders or, for clays, deliberately creating it (Section 2.5), and removing cements such as carbonate where needed.

1.4 Electron beam methods: SEM, EDS and the electron microprobe

Interactions of an electron beam with a sample. When a focused beam of electrons, accelerated by 10 to 30 kV, strikes a solid, the electrons penetrate and scatter within a pear-shaped **interaction volume** about 1 to 5 μm across (Figure 1.4). Several signals are produced:

- **Secondary electrons** (SE), of low energy, escape only from the top few nanometres of the surface. They show the **topography** of the sample and give the familiar high-resolution SEM images of grains and fossils.
- **Backscattered electrons** (BSE) are beam electrons scattered back out of the sample. Their number increases with the mean atomic number of the material, so BSE images show **compositional contrast**: heavy minerals such as galena, zircon and monazite appear bright and light minerals such as quartz and clays appear dark.
- **Characteristic X-rays** are emitted from the whole interaction volume and identify and measure the elements present.
- Other signals include **cathodoluminescence** (visible light, which reveals growth zoning in quartz, zircon and carbonates) and continuous X-rays.

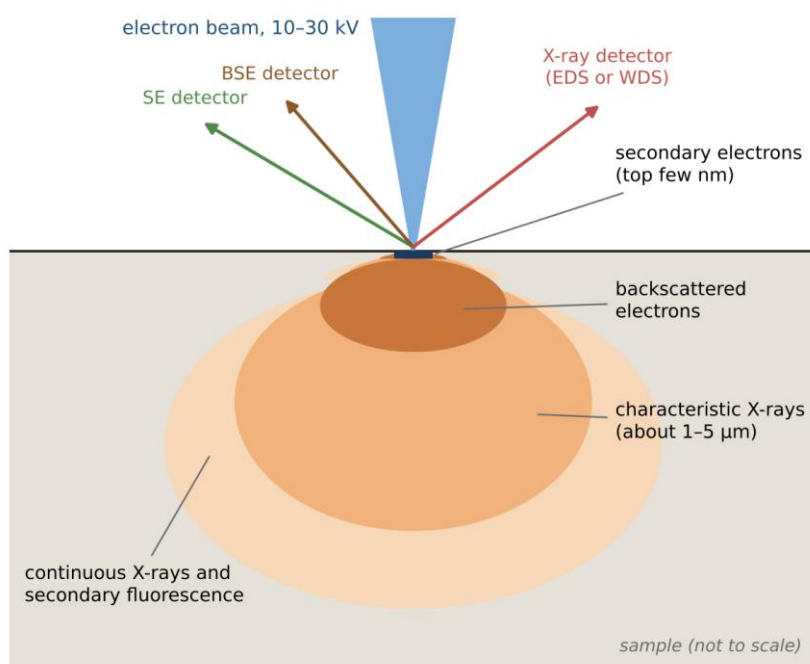


Figure 1.4. Interaction of an electron beam with a sample: secondary electrons come from the surface, backscattered electrons from a deeper zone, and characteristic X-rays from most of the interaction volume.

The depth of the interaction volume can be estimated from the **Kanaya-Okayama range**:

$$R (\mu\text{m}) = \frac{0.0276 A E_0^{1.67}}{Z^{0.89} \rho}$$

where A is the atomic weight (g/mol), E_0 the beam energy (keV), Z the atomic number and ρ the density (g/cm³). For silicon ($A = 28.09$, $Z = 14$, $\rho = 2.33$) at 15 keV, $R \approx 2.9 \mu\text{m}$, and at 25 keV about $6.9 \mu\text{m}$. The spatial resolution of X-ray analysis is therefore about 1 to 3 μm , much coarser

than that of SE images. Grains smaller than this cannot be analysed without contributions from their neighbours.

The scanning electron microscope (SEM). In an SEM, the beam is scanned across the sample in a raster, and the signal from each point builds up an image. Samples must be conductive, so non-conducting minerals are coated with a thin film of carbon or gold. SEMs are used for:

- imaging the shapes and surfaces of grains, microfossils, clay fabrics and pores in sediments and reservoir rocks;
- BSE imaging of polished sections to map minerals by their brightness;
- rapid chemical analysis and element mapping by EDS.

Energy-dispersive spectrometry (EDS). An EDS detector, a semiconductor crystal (now usually a silicon drift detector), records all the X-rays arriving at once and sorts them by energy. In a minute or less it produces a spectrum showing all elements from boron or carbon to uranium. Its main limitations are its **energy resolution** of about 130 eV, which causes nearby peaks to overlap, and a detection limit of about 0.1 wt%.

Wavelength-dispersive spectrometry (WDS). A WDS spectrometer uses a crystal of known d-spacing to diffract the X-rays, according to Bragg's law, into a detector. Only one wavelength is measured at a time, chosen by setting the angle of the crystal. The energy resolution is about 10 eV, more than ten times better than EDS, and peak-to-background ratios are much higher, giving detection limits of about 100 ppm. The difference matters where peaks overlap (Figure 1.5): for example, the S K α (2.307 keV) and Pb M α (2.346 keV) lines of galena are only about 40 eV apart, and S K α and Mo L α (2.293 keV) in molybdenite only about 14 eV apart.

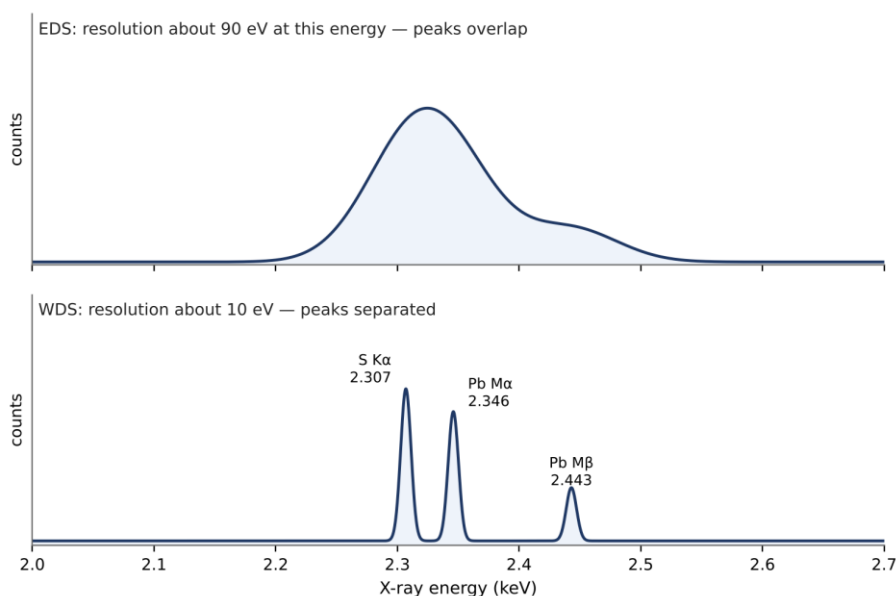


Figure 1.5. The same part of the X-ray spectrum of galena (PbS) recorded by EDS and by WDS (schematic). The S K α and Pb M α lines overlap in the EDS spectrum but are separated by WDS.

The electron probe microanalyser (EPMA). The electron microprobe is an instrument optimised for accurate quantitative analysis, with four or five WDS spectrometers, an optical microscope and a very stable beam. It analyses polished, flat, carbon-coated samples, comparing the intensity of each characteristic line with that from a **standard** of known composition. The measured ratios are then converted to concentrations by **matrix corrections**, known as **ZAF** corrections, for the effects of atomic number (Z), absorption (A) and fluorescence (F) within the sample. Accuracies of 1–2% of the amount present are obtained for major elements. Results are

reported as weight per cent of the oxides for silicates and oxides, or of the elements for sulphides and alloys. Light elements (H, Li, Be) cannot be measured, and the oxidation state of iron is not determined directly, so Fe is usually reported as FeO. Water and carbonate are not measured either, so analyses of micas, amphiboles and carbonates have totals less than 100%.

1.5 Calculating a mineral formula from an analysis

A microprobe analysis gives weight per cent oxides. To turn it into a **mineral formula**, the number of cations is calculated on the basis of a fixed number of oxygen atoms in the formula: 4 for olivine, 6 for pyroxene, 8 for feldspar and 12 for garnet. The steps are:

1. Divide the weight per cent of each oxide by its molecular weight to obtain the number of moles of the oxide.
2. Multiply by the number of oxygens in the oxide (2 for SiO₂, 1 for MgO, 3 for Al₂O₃) to obtain the moles of oxygen; add them up.
3. Calculate the **normalisation factor**: the number of oxygens in the formula divided by the total moles of oxygen.
4. Multiply the moles of each cation (moles of oxide × cations per oxide) by this factor.

$$\text{Cations per formula unit} = \frac{w_i}{M_i} \times n_{\text{cat},i} \times \frac{N_o}{\sum_j (w_j n_{o,j} / M_j)}$$

Worked example: olivine. An olivine from a basalt gives the following analysis. The formula is calculated on the basis of 4 oxygens:

Oxide	wt%	Molecular weight	Moles of oxide	Moles of O	Cations per 4 O
SiO ₂	40.20	60.08	0.6691	1.3381	Si 0.990
FeO	10.10	71.84	0.1406	0.1406	Fe 0.208
MnO	0.15	70.94	0.0021	0.0021	Mn 0.003
MgO	49.05	40.30	1.2170	1.2170	Mg 1.801
NiO	0.38	74.69	0.0051	0.0051	Ni 0.008
Total	99.88			2.7029	3.010

The normalisation factor is $4/2.7029 = 1.480$. The formula is (Mg_{1.80}Fe_{0.21}Ni_{0.01})Si_{0.99}O₄, close to the ideal (Mg, Fe)₂SiO₄ with 3 cations and 1 Si per 4 oxygens, which confirms that the analysis is good. The composition is expressed as the forsterite content:

$$\text{Fo} = 100 \times \frac{\text{Mg}}{\text{Mg} + \text{Fe}} = 100 \times \frac{1.801}{1.801 + 0.208} \approx 90$$

so the olivine is Fo₉₀, typical of the mantle and of primitive basalts.

1.6 X-ray fluorescence and other methods

X-ray fluorescence (XRF). In XRF, the sample is irradiated with X-rays from a tube, which knock out inner-shell electrons and cause the atoms to emit their own characteristic X-rays, called fluorescence. These are measured by a crystal spectrometer (wavelength-dispersive XRF) or an energy-dispersive detector (EDXRF). Because the volume analysed is large, XRF gives the **bulk composition** of a rock, sediment or ore. For accurate analysis of major elements, the powdered sample is fused with a lithium borate flux into a glass bead, removing the effects of

grain size and mineralogy; for trace elements, pressed powder pellets are used. The **loss on ignition** (LOI), measured by heating the sample to about 1,000 °C, accounts for water, carbonate and organic matter. Major elements are reported as oxides (SiO₂, Al₂O₃, Fe₂O₃, CaO and so on) and trace elements in ppm. **Portable XRF** instruments give rapid, if less accurate, analyses in the field and core store, and are widely used in mineral exploration and in screening sediments for metal pollution.

Other methods. Several other methods complete the toolkit:

Method	Principle	Main uses
ICP-OES and ICP-MS	Sample dissolved and sprayed into an argon plasma; emitted light or ions measured	Major and trace elements in rocks, sediments and waters, to ppb levels
Laser ablation ICP-MS	Laser spot (10–100 µm) on a section feeds the ICP-MS	Trace elements in single grains; U–Pb dating of zircon and monazite
Raman and infrared (FTIR) spectroscopy	Vibrations of bonds in the crystal	Identification of small grains, inclusions, polymorphs, carbonates and clays
Thermal analysis (DTA, TGA)	Weight loss and heat flow on heating	Clays, carbonates, hydrous minerals; water content
Mössbauer spectroscopy	Nuclear resonance of ⁵⁷ Fe	Fe ²⁺ /Fe ³⁺ ratio in minerals
Automated mineralogy (QEMSCAN, MLA)	SEM with BSE and EDS mapping of thousands of grains	Modal mineralogy, grain size and liberation of ores and sediments

Choosing a method. The choice depends on the question. To identify the minerals in a clay or a fine-grained sediment, XRD is the first method. To determine how composition varies within and between grains, use SEM-EDS for a quick answer or EPMA for accurate data. For the bulk chemistry of many samples, use XRF or ICP. Very often several methods are combined: for example, a heavy mineral sand might be studied by XRF for bulk TiO₂ and ZrO₂, XRD for its minerals, and automated SEM for the grain size and liberation of ilmenite, rutile and zircon.

1.7 Key points of Section 1

- X-rays are produced as continuous radiation and as characteristic lines whose energies identify the element (Moseley's law).
- Bragg's law, $n\lambda = 2d\sin\theta$, relates diffraction angles to the spacing of lattice planes; powder XRD identifies minerals and estimates their proportions and crystallite size.
- An electron beam produces secondary electrons (topography), backscattered electrons (composition contrast) and characteristic X-rays (chemistry) from an interaction volume of a few micrometres.
- EDS is fast and shows all elements; WDS has much better resolution and detection limits; the electron microprobe gives accurate analyses after ZAF corrections.
- Mineral formulae are calculated from oxide analyses by normalising to a fixed number of oxygens.
- XRF gives bulk major and trace element chemistry; ICP-MS, Raman, thermal analysis and automated mineralogy complete the toolkit.

Section 2: Clay minerals and marine authigenic minerals

2.1 What are clay minerals?

The word **clay** has two meanings. As a **size** term, clay is the fraction of a sediment or soil finer than $2\ \mu\text{m}$ (some engineers use $4\ \mu\text{m}$ or $2\ \mu\text{m}$). As a **mineral** term, the **clay minerals** are a group of hydrous **phyllosilicates** (sheet silicates) that are typically very fine-grained and form mostly at or near the Earth's surface by weathering, diagenesis or low-temperature hydrothermal alteration. Most of the clay-size fraction of sediments is made of clay minerals, but it may also contain fine quartz, feldspar, carbonates, iron oxides and organic matter.

Clay minerals matter to the marine geologist because they:

- make up most of the mud that covers the continental shelves, slopes and deep ocean floor;
- record the climate and weathering on land, and the sources and pathways of sediment;
- control the plasticity, swelling, strength and permeability of soils and mudrocks, and so the behaviour of seabed foundations and slopes;
- form seals and affect the quality of petroleum reservoirs, and change with burial in sedimentary basins such as the Niger Delta;
- adsorb metals, nutrients and pollutants, and are raw materials for industry.

2.2 Structure of the clay minerals

All clay minerals are built from two kinds of sheets (Figure 2.1):

- The **tetrahedral sheet** (T) consists of SiO_4 tetrahedra, each sharing three basal oxygens with neighbouring tetrahedra to form a hexagonal network, with composition Si_2O_5 . Some Si^{4+} may be replaced by Al^{3+} , creating a negative charge.
- The **octahedral sheet** (O) consists of cations, mainly Al^{3+} , Mg^{2+} or Fe, each surrounded by six oxygens or hydroxyls. If the cations are trivalent (Al^{3+}), only two out of every three octahedral sites are filled, as in gibbsite, $\text{Al}(\text{OH})_3$: the sheet is **dioctahedral**. If they are divalent (Mg^{2+} , Fe^{2+}), all three sites are filled, as in brucite, $\text{Mg}(\text{OH})_2$: the sheet is **trioctahedral**.

The sheets are joined, by sharing the apical oxygens of the tetrahedra, into **layers** of two types:

- **1:1 layers** (TO): one tetrahedral and one octahedral sheet, about $7\ \text{\AA}$ thick. Adjacent layers are held together by hydrogen bonds. Example: kaolinite.
- **2:1 layers** (TOT): an octahedral sheet between two tetrahedral sheets, about $9.5\ \text{\AA}$ thick. The space between successive layers, the **interlayer**, may be empty (pyrophyllite, talc), or contain cations (K^+ in illite and micas), exchangeable hydrated cations and water (smectite, vermiculite), or a complete octahedral hydroxide sheet (chlorite).

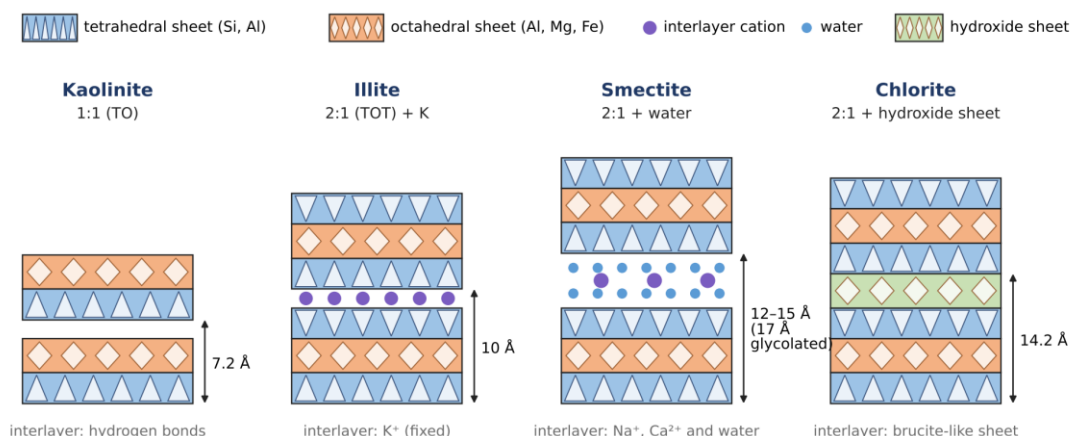


Figure 2.1. The building blocks of clay minerals: the tetrahedral (T) and octahedral (O) sheets combine into 1:1 layers (kaolinite, 7 Å) and 2:1 layers, whose interlayer contents give the basal spacings of illite (10 Å), smectite (12–15 Å, swelling to 17 Å) and chlorite (14 Å).

Layer charge. Substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet, or of Mg^{2+} for Al^{3+} in the octahedral sheet, leaves the 2:1 layer with a net negative charge, x , expressed per formula unit of $\text{O}_{10}(\text{OH})_2$. This charge is balanced by cations in the interlayer. The layer charge is the main basis for classifying the 2:1 clays: about 0.2–0.6 in smectites, 0.6–0.9 in vermiculites and illites, and about 1 in true micas. Low-charge layers hold their interlayer cations weakly, so these can be exchanged and water can enter, causing swelling. High-charge layers hold K^+ strongly and do not swell.

Basal spacing. The repeat distance from one layer to the next, perpendicular to the layers, is the **basal spacing**, d_{001} . It is the most important property for identifying clays by XRD (Section 2.5).

2.3 The main groups of clay minerals

Group	Layer type	Ideal or typical formula	d_{001} (Å)	Notes
Kaolinite (kaolin)	1:1, dioctahedral	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	7.1–7.2	Includes halloysite (10 Å when hydrated); forms by intense weathering
Serpentine and berthierine	1:1, trioctahedral	$(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$	7.1	Berthierine and odinite are Fe-rich marine varieties
Illite	2:1, dioctahedral	$\text{K}_{0.75}\text{Al}_2(\text{Si}_{3.25}\text{Al}_{0.75})\text{O}_{10}(\text{OH})_2$	10	Fine-grained, K-deficient mica; glauconite is an Fe-rich equivalent
Smectite	2:1, di- or trioctahedral	$(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	12–15	Montmorillonite, beidellite, nontronite, saponite; swells
Vermiculite	2:1, mainly trioctahedral	$\text{Mg}_{0.7}(\text{Mg,Fe,Al})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	14	Higher charge than smectite; limited swelling
Chlorite	2:1 + hydroxide sheet	$(\text{Mg,Fe,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$	14	Interlayer brucite-like sheet; does not swell

Group	Layer type	Ideal or typical formula	d_{001} (Å)	Notes
Mixed-layer clays	Interstratified	e.g. illite–smectite (I/S)	Varies	Common in buried mudrocks and soils
Palygorskite and sepiolite	Modulated 2:1 ribbons	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ (sepiolite)	10.5, 12.2	Fibrous; arid soils, lakes and saline lagoons

2.4 Properties of the clay minerals

Cation exchange capacity (CEC). Because of their layer charge and broken edges, clays hold cations that can be exchanged with those in the surrounding water. The CEC is measured in milliequivalents per 100 g of dry clay (meq/100 g, numerically the same as cmol/kg). If the CEC comes mainly from the permanent layer charge, it can be estimated as:

$$\text{CEC (meq/100 g)} = \frac{x}{M} \times 10^5$$

where x is the layer charge per formula unit and M is the formula weight (g/mol).

Worked example: CEC of montmorillonite. For $\text{Na}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$, $x = 0.33$ and $M \approx 367$ g/mol, so

$$\text{CEC} = \frac{0.33}{367} \times 10^5 \approx 90 \text{ meq/100 g}$$

which falls within the measured range for smectites (Figure 2.2). Kaolinite, with almost no layer charge, has a CEC of only a few meq/100 g, mainly from its edges.

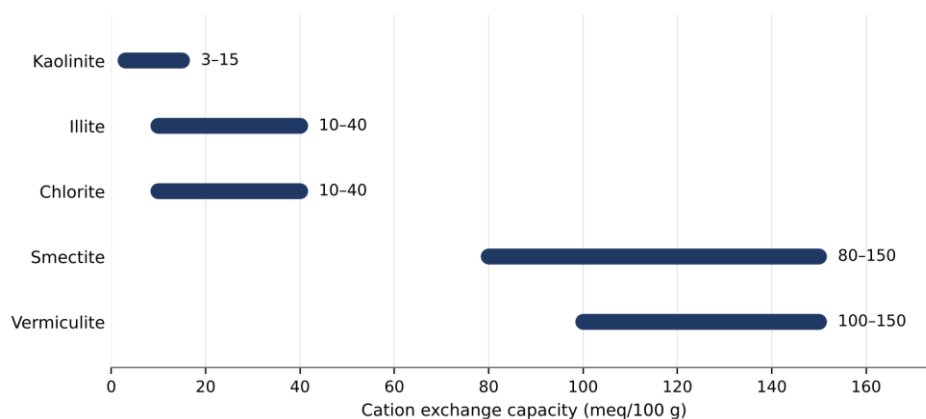


Figure 2.2. Typical ranges of cation exchange capacity of the clay mineral groups. The swelling clays, smectite and vermiculite, have by far the highest values.

Specific surface area and swelling. Smectites have very small, thin particles and an internal surface between the layers, giving specific surface areas of up to about 800 m²/g, compared with 10–20 m²/g for kaolinite. Water enters the interlayers of smectite, especially with Na⁺ as the exchangeable cation, so the clay swells strongly when wetted and shrinks on drying.

Plasticity and engineering behaviour. The same properties make smectite-rich soils highly plastic, compressible and weak, with high liquid limits and low permeability. Expansive soils, such as the black cotton soils of north-eastern Nigeria, damage roads and buildings by swelling and shrinking with the seasons. Marine muds rich in smectite and illite form the soft, compressible clays of deltas and continental shelves, which govern the design of foundations, pipelines and offshore structures.

Adsorption. Clays adsorb heavy metals, nutrients, radionuclides and organic pollutants, so the clay-rich muds of estuaries and harbours become sinks for contaminants. This is one reason why dredged harbour muds must be tested before disposal.

2.5 Identifying clay minerals by X-ray diffraction

Because clay particles are tiny and platy, they are best identified on **oriented mounts**. The clay fraction (less than 2 μm) is separated from the sediment by dispersion in water and settling or centrifuging, after removal of carbonate (with dilute acetic acid or buffered acetate) and organic matter (with hydrogen peroxide) if necessary. A suspension of the clay is dried on a glass slide, so that the flakes lie flat. The XRD pattern of an oriented mount is then dominated by the basal (00 l) reflections, which give d_{001} and its higher orders.

Because several groups have similar basal spacings (7 Å for kaolinite and the second order of chlorite; 14 Å for chlorite, vermiculite and smectite), each sample is examined after a standard sequence of **treatments** (Figure 2.3):

1. **Air-dried (AD).**
2. **Ethylene glycol solvated (EG):** glycol enters the interlayers of smectite, which expands to about 17 Å.
3. **Heated to 400 °C** for one hour: the interlayer water of smectite and vermiculite is driven off and they collapse to about 10 Å.
4. **Heated to 550 °C:** kaolinite loses its structure and its peaks disappear; chlorite remains at 14 Å, with its first-order peak strengthened.

Mineral	Air-dried	Glycolated	400 °C	550 °C
Kaolinite	7.1–7.2 Å	No change	No change	Destroyed (no peak)
Illite	10 Å	10 Å	10 Å	10 Å
Smectite	12–15 Å	about 17 Å	about 10 Å	about 10 Å
Vermiculite	about 14 Å	14 Å (Mg form)	about 10 Å	about 10 Å
Chlorite	14 Å (and 7, 4.7, 3.5 Å)	No change	No change	14 Å, stronger
Mixed-layer illite–smectite	Between 10 and 15 Å	Between 10 and 17 Å	10 Å	10 Å

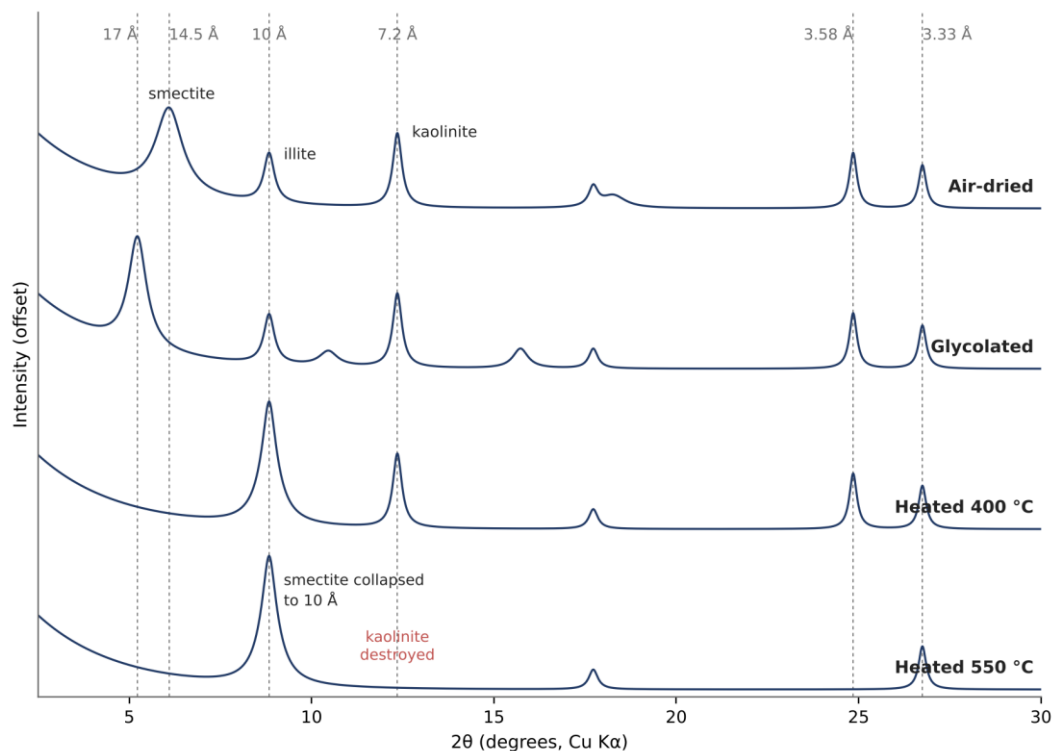


Figure 2.3. Schematic XRD patterns of an oriented clay mount containing smectite, illite and kaolinite, after the standard treatments (Cu K α). The smectite peak moves to 17 Å on glycolation and to 10 Å on heating; the kaolinite peak at 7.2 Å disappears at 550 °C.

Worked example: peak positions. With Cu K α , a basal spacing of 17 Å gives a peak at

$$2\theta = 2\arcsin\left(\frac{\lambda}{2d}\right) = 2\arcsin\left(\frac{1.5406}{34}\right) = 5.19^\circ$$

while 10 Å gives 8.84° and 7.16 Å gives 12.35°. The low angles of clay peaks are why patterns of oriented mounts are recorded from as low as 2° or 3° 2 θ .

Two further tests help. Kaolinite and chlorite can also be distinguished at 7 Å by the separate peaks of kaolinite (002) at 3.58 Å and chlorite (004) at 3.54 Å. **Dioctahedral** and **trioctahedral** clays are distinguished by the (060) reflection in a random powder: about 1.49–1.50 Å for dioctahedral clays (kaolinite, illite, montmorillonite) and 1.53–1.54 Å for trioctahedral clays (chlorite, saponite, vermiculite). The proportions of the clay groups are estimated semi-quantitatively from the areas of their basal peaks on the glycolated pattern, using weighting factors.

2.6 Origin of clay minerals and their distribution in the oceans

Clay minerals in marine sediments have three main origins:

- **Detrital (inherited)** clays formed on land by weathering and carried to the sea by rivers, wind and ice. This is by far the largest source.
- **Neoformed or transformed** clays formed or altered within the sea or within the sediment after deposition, such as smectite from the alteration of volcanic ash and glauconite on the shelf.
- **Diagenetic** clays formed during burial, such as illite and chlorite.

Climate control on weathering. On land, the clay mineral produced depends on climate, drainage and parent rock. Intense chemical weathering in hot, humid climates with good

drainage leaches silica and bases and produces **kaolinite**, together with gibbsite and iron oxides in laterites, as on the crystalline basement and sedimentary basins of southern Nigeria. Poor drainage, seasonal climates and basic rocks favour **smectite**, as in the black cotton soils of the Chad Basin. In cold and arid regions, where physical weathering dominates, the clays are mainly **illite and chlorite** inherited from the parent rocks.

Distribution in the oceans. As a result, the clay minerals of deep-sea sediments show a broad pattern with latitude, first mapped in the 1960s:

- **kaolinite** is most abundant in tropical latitudes, off the great tropical rivers of Africa, South America and Asia, including the Gulf of Guinea;
- **chlorite** is most abundant in polar and high latitudes, where physical weathering and glacial erosion dominate;
- **illite** is the most abundant clay overall, especially in the North Atlantic and North Pacific, supplied by rivers and wind-blown dust;
- **smectite** is abundant where volcanic material is altered, especially in the South Pacific and around volcanic islands and ridges.

Wind also carries clay. Saharan dust, blown across West Africa by the Harmattan and over the tropical Atlantic, adds illite, kaolinite and fibrous palygorskite to the sediments. Because the clay assemblage reflects climate on land, changes in clay minerals in sediment cores are used to reconstruct past climates and monsoon strength.

Burial diagenesis. As muds are buried, smectite is progressively transformed into illite through mixed-layer illite–smectite, mainly at temperatures of about 60 to 120 °C. The reaction consumes potassium, releases water and silica, and can contribute to overpressure, so it is important in thick deltaic successions such as the Niger Delta. The proportion of illite layers in I/S is used as an indicator of the maximum temperature reached by a mudrock, alongside vitrinite reflectance. With further burial, kaolinite in sandstones may be replaced by illite or dickite, and chlorite coatings on sand grains can preserve porosity by preventing quartz cement.

2.7 Authigenic minerals in marine sediments

Authigenic minerals are those that form in place, in the water column or within the sediment, rather than being transported from elsewhere. Their formation depends on water depth, sedimentation rate, the supply of organic matter and the chemistry of the water and pore water. Figure 2.4 shows where the main ones form across a continental margin.

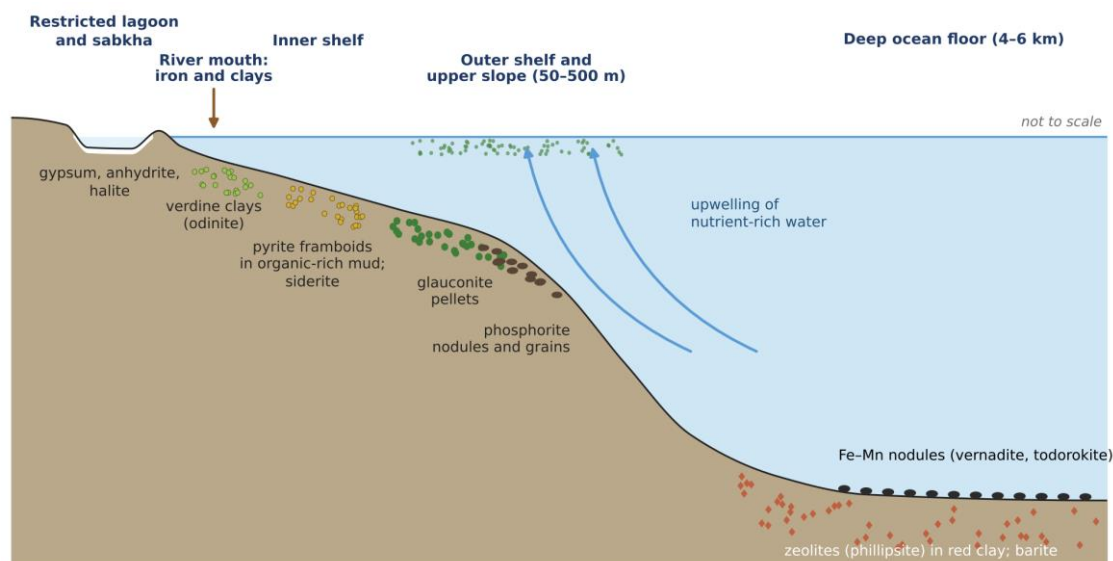


Figure 2.4. Where the main authigenic minerals form across a continental margin: evaporites in restricted lagoons, verdine clays near tropical river mouths, pyrite in organic-rich muds, glauconite and phosphorite on the outer shelf and upper slope, and zeolites, barite and ferromanganese oxides on the deep ocean floor.

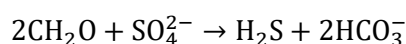
Glauconite is a green, K- and Fe^{3+} -rich dioctahedral 2:1 clay mineral (a member of the mica group in the broad sense) with an ideal formula close to $\text{K}(\text{Fe}^{3+}, \text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$. It occurs as sand-sized green **pellets** (glauconitic grains) that form by the alteration of faecal pellets, fragments of minerals, or the infilling of foraminiferal tests. It forms on the outer continental shelf and upper slope, at water depths of about 50 to 500 m, in slightly reducing conditions just below the sediment–water interface, where sedimentation is very slow. As the grains mature, their K_2O content increases, from less than 4% in “nascent” glauconite to more than 8% in “highly evolved” glauconite, over hundreds of thousands to about a million years. Glauconite is therefore a marker of **condensed sections** and marine flooding surfaces in sequence stratigraphy. It is used, with care, for K–Ar and Rb–Sr dating, and glauconitic sands (“greensands”) are used as slow-release potash fertilisers.

Verdine facies clays (odinite and related Fe-rich 7 Å minerals) form in tropical shelf waters at shallower depths, typically less than about 60 m, near the mouths of rivers that supply iron, including on the shelves of West Africa.

Phosphorite is a sedimentary rock rich in **carbonate fluorapatite** (francolite), approximately $\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3\text{F}$. It forms where large amounts of organic matter reach the seabed, typically under zones of **coastal upwelling** on western continental margins, such as off Namibia, Peru and Morocco. Phosphate released by the decay of organic matter in the upper sediment precipitates as apatite, and repeated reworking by currents winnows away the fine sediment and concentrates the phosphatic grains and nodules. Phosphorite is the main source of phosphate fertiliser; Morocco holds about two-thirds of the world’s reserves. Nigeria has sedimentary phosphate deposits of Palaeogene age at Oshosun in Ogun State and in the Sokoto Basin.

Zeolites are framework aluminosilicates with large open channels containing water and exchangeable cations. In marine sediments, **phillipsite** forms from the alteration of basaltic glass in the slowly accumulating red clays of the Pacific, and **clinoptilolite** from silicic volcanic ash and biogenic silica. Zeolites are used as ion exchangers, molecular sieves and absorbents.

Pyrite forms in organic-rich, anoxic muds where bacteria reduce sulphate in pore water to H_2S , which reacts with iron:



The iron monosulphides formed first are converted to pyrite, often as raspberry-like **framboids** a few micrometres across. Pyrite records anoxic or euxinic conditions. When pyritic mangrove and estuarine muds, such as those of the Niger Delta, are drained or dredged and exposed to air, the pyrite oxidises to sulphuric acid, creating **acid sulphate soils** that damage crops, concrete and steel.

Other authigenic minerals include:

- **carbonates:** aragonite and high-Mg calcite cements and ooids in warm shallow seas, dolomite in sabkhas and during burial, siderite concretions in delta muds, and carbonates at cold seeps where methane is oxidised;
- **evaporites:** gypsum, anhydrite and halite in restricted lagoons, sabkhas and isolated basins, which form important seals and salt structures, as in the Aptian salt basins of the West African margin from Gabon to Angola;
- **barite:** microcrystalline barite in pelagic sediments beneath areas of high productivity, used as an indicator of past productivity, and barite at cold seeps and hydrothermal vents;
- **iron–manganese oxyhydroxides:** vernadite, birnessite and todorokite in manganese nodules and crusts on the deep seafloor, which concentrate Mn, Ni, Cu and Co (MGY 405).

Mineral	Composition	Typical setting	Significance
Glaucanite	K–Fe ³⁺ 2:1 clay	Outer shelf, upper slope (50–500 m); slow sedimentation	Condensed sections; dating; fertiliser
Verdine (odinite)	Fe-rich 7 Å clay	Tropical inner shelf near river mouths	Warm-water shelf indicator
Phosphorite (francolite)	Carbonate fluorapatite	Upwelling margins; outer shelf and slope	Phosphate fertiliser; productivity
Pyrite	FeS ₂	Anoxic organic-rich muds	Redox indicator; acid sulphate soils
Phillipsite, clinoptilolite	Zeolites	Pelagic clays, altered ash	Volcanic input; industrial uses
Gypsum, anhydrite, halite	Sulphates, chloride	Restricted lagoons and basins	Seals; salt tectonics
Barite	BaSO ₄	Pelagic sediments, seeps, vents	Productivity proxy
Vernadite, todorokite	Mn–Fe oxyhydroxides	Abyssal plains, seamounts	Ni, Cu, Co, Mn resources

2.8 Clays as resources

Clays and authigenic minerals are important industrial minerals:

- **Kaolin** is used in ceramics, paper coating, paint, rubber, plastics and pharmaceuticals. Nigeria has large kaolin resources, for example at Kankara in Katsina State, formed by the weathering of granites and feldspathic sediments.
- **Bentonite**, a rock composed mainly of smectite formed from altered volcanic ash, is used in drilling muds, foundry sands, iron-ore pelletising, sealing of landfills and dams,

and as an absorbent. Nigeria imports most of the bentonite used in oil and gas drilling, and local bentonitic clays are being studied as substitutes, which requires careful characterisation of their smectite content, exchangeable cations and swelling by the methods of Sections 1 and 2.

- **Palygorskite and sepiolite** are used as absorbents and in drilling muds for salt-water environments.
- **Zeolites** are used in water treatment, animal feed and pollution control, and **phosphorite** and **glauconite** as fertilisers.

2.9 Key points of Section 2

- Clay minerals are hydrous phyllosilicates built of tetrahedral and octahedral sheets arranged in 1:1 (7 Å) or 2:1 layers; the interlayer contents give basal spacings of 10 Å (illite), 12–15 Å (smectite) and 14 Å (chlorite, vermiculite).
- Layer charge controls cation exchange capacity, swelling and plasticity; smectites have the highest CEC and swelling.
- Clays are identified by XRD of oriented mounts after air-drying, glycolation and heating to 400 °C and 550 °C.
- Detrital clays in the oceans reflect weathering on land: kaolinite in the tropics, chlorite at high latitudes, illite widely, smectite near volcanic sources; smectite changes to illite with burial.
- Authigenic minerals, including glauconite, phosphorite, pyrite, zeolites, evaporites, barite and Fe–Mn oxides, record the depth, sedimentation rate and chemistry of their environment, and several are valuable resources.

Section 3: Ore mineralogy

3.1 Scope and uses of ore mineralogy

Ore mineralogy is the study of the minerals of ore deposits: their identification, composition, textures and relationships. Most ore minerals, including the sulphides, sulpharsenides, native metals and many oxides, are **opaque**: they absorb light so strongly that they appear black in thin section under transmitted light. They are therefore studied in **reflected light**, on polished surfaces, with the **ore microscope** (also called the reflected-light or metallurgical microscope).

Ore mineralogy is used to:

- identify the ore and gangue minerals and estimate their proportions;
- interpret the **textures** and the sequence of formation (**paragenesis**) of minerals, and so the origin of the deposit;
- determine the grain size and intergrowths of valuable minerals, which control how finely the ore must be ground to free them (**liberation**) and how it can be processed;
- recognise minerals that cause problems in processing or the environment, such as arsenopyrite, pyrrhotite and clay minerals;
- guide the choice of grains for electron microprobe, LA-ICP-MS or automated mineralogy (Section 1).

3.2 The ore microscope and sample preparation

Polished sections. Samples are mounted in epoxy resin as **polished blocks** (typically 25–30 mm across) or prepared as **polished thin sections**, which can be examined in both transmitted and reflected light. The surface is ground flat and then polished with progressively finer diamond pastes, down to 1 μm or less. A good polish, free of scratches and relief, is essential, because the optical properties are observed on the surface. Loose grains, such as heavy mineral concentrates or mill products, are mounted in resin and polished in the same way.

The microscope. The ore microscope has the same stage, objectives, polariser and analyser as the transmitted-light microscope, but light from the lamp enters from the side, above the objective. A **vertical illuminator** (a half-silvered plate or prism) directs it down through the objective onto the polished surface, and the reflected light returns up through the objective to the eyepiece (Figure 3.1). Observations are made:

- in **plane-polarised light** (PPL), with the polariser only, to see colour, reflectance, bireflectance and hardness;
- with **crossed polars** (XPL), with the analyser inserted, to see anisotropy and internal reflections.

Objectives can be used dry, in air, or with **immersion oil**, which increases contrast and enhances colour differences and internal reflections.

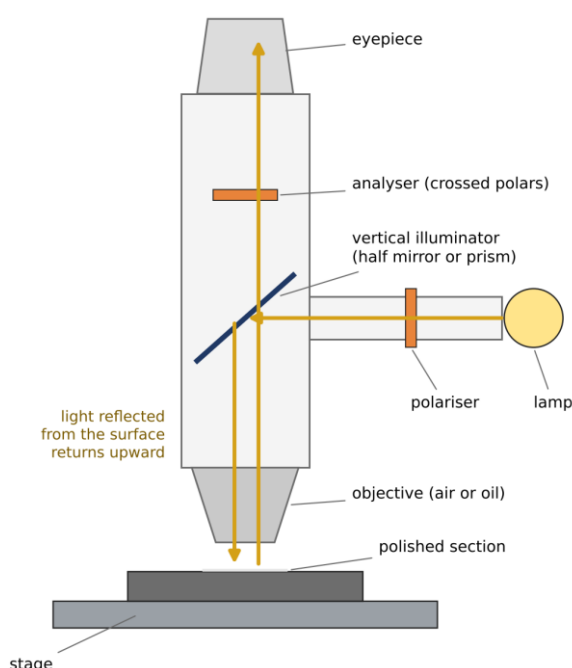


Figure 3.1. Light path in the reflected-light (ore) microscope. Light from the lamp is polarised, turned down through the objective by the vertical illuminator, reflected from the polished section, and returns through the analyser to the eyepiece.

3.3 Optical and physical properties in reflected light

Colour. In reflected light, most ore minerals are white, grey or pale shades, and colours are best judged by comparing adjacent minerals. Some have distinctive colours: gold is bright yellow, chalcopyrite brass yellow, pyrite pale yellowish white, bornite pinkish brown (tarnishing purple), covellite deep blue, pyrrhotite creamy pinkish brown, and galena pure white. Magnetite is grey with a brownish tint, sphalerite and cassiterite are darker grey.

Reflectance. The **reflectance**, R , is the percentage of incident light that is reflected from the polished surface. It is the most important quantitative property. For a mineral with refractive index n and absorption coefficient k , observed in a medium of refractive index N , the Fresnel equation gives:

$$R = \frac{(n - N)^2 + k^2}{(n + N)^2 + k^2}$$

with $N = 1.000$ in air and $N \approx 1.515$ in immersion oil. Transparent minerals have $k \approx 0$, so their reflectance is low. Strongly absorbing minerals have large k and high reflectance.

Worked example: reflectance of sphalerite. Sphalerite has $n \approx 2.37$ and $k \approx 0$. In air:

$$R = \frac{(2.37 - 1)^2}{(2.37 + 1)^2} = \frac{1.877}{11.36} \approx 16.5\%$$

In oil, with $N = 1.515$, $R = (0.855)^2 / (3.885)^2 \approx 4.8\%$. The reflectance of transparent minerals falls much more in oil than that of strongly absorbing minerals such as pyrite, which is why oil immersion increases the contrast between them.

Reflectance is measured with a photometer or digital camera attached to the microscope, by comparing the intensity of light reflected from the mineral, I_m , with that from a **standard** of known reflectance, R_s , such as silicon carbide or tungsten–titanium carbide:

$$R_m = R_s \times \frac{I_m}{I_s}$$

Reflectance varies with the wavelength of light (its variation gives the colour of the mineral) and, for anisotropic minerals, with orientation. Values are usually quoted for green light at 546 nm or yellow light at 589 nm. The common ore minerals span a wide range (Figure 3.2).

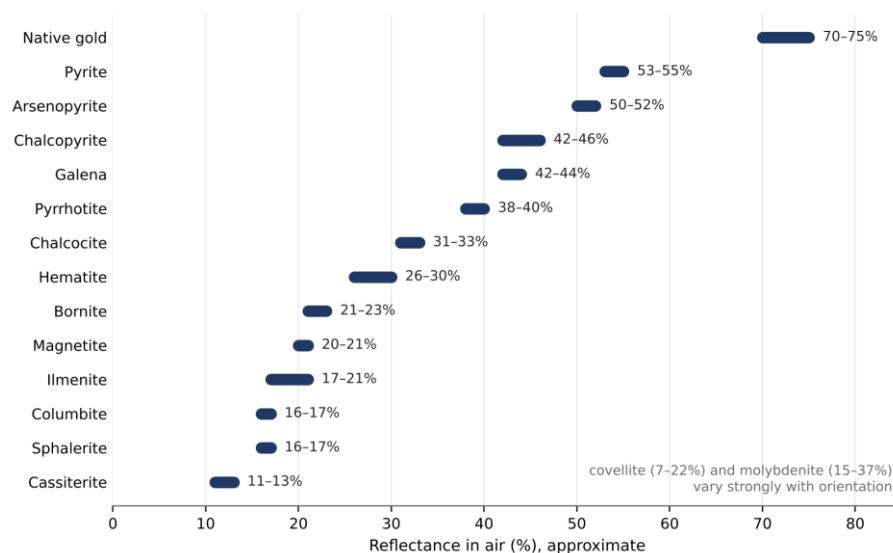


Figure 3.2. Approximate reflectance in air of common ore minerals. Transparent minerals such as cassiterite and sphalerite have low reflectance; pyrite and native gold are among the brightest.

Bireflectance and reflection pleochroism. In anisotropic minerals, the reflectance and colour change as the stage is rotated in PPL. A change in brightness is **bireflectance**, and a change in colour is **reflection pleochroism**. They are strong in covellite (deep blue to bluish white), molybdenite, graphite and stibnite, and weak or absent in most other minerals.

Anisotropy. With crossed polars, minerals of the cubic system and amorphous materials remain dark (or uniformly grey) as the stage is rotated: they are **isotropic**. Pyrite, galena, sphalerite, magnetite, chromite and native gold are isotropic. Minerals of lower symmetry are generally **anisotropic** and show changes in brightness and colour, with four positions of darkness or minimum brightness in each rotation. Anisotropy is strong in hematite, ilmenite, pyrrhotite, marcasite, arsenopyrite, molybdenite, graphite and covellite, whose anisotropy colours are a brilliant orange. Chalcopyrite is weakly anisotropic.

Internal reflections. In minerals that are partly transparent, light penetrates the surface and is reflected back from cracks, cleavages and grain boundaries below it, appearing as coloured light within the grain. **Internal reflections** are best seen with crossed polars and oil immersion, and their colour is diagnostic: yellow to brown in sphalerite, yellowish to brown in cassiterite, deep red in cinnabar and hematite (in thin flakes), red-brown in columbite and rutile, and white or colourless in quartz, carbonates and other gangue minerals.

Hardness. Three measures of hardness are used:

- **Polishing hardness** is shown by **relief**: harder minerals stand slightly above softer ones on the polished surface. When the distance between the objective and the section is increased slightly, a thin bright line (the Kalb line) moves into the softer of two adjacent minerals.
- **Scratch hardness** is shown by how readily a mineral is scratched during polishing; soft minerals such as galena and gold are scratched easily.
- **Micro-indentation hardness** is measured with a diamond pyramid pressed into the surface under a known load. The **Vickers hardness number** is

$$\text{VHN} = \frac{1.8544 P}{d^2}$$

where P is the load in kilograms-force and d is the mean diagonal of the indentation in millimetres; VHN is expressed in kg/mm^2 .

Worked example: Vickers hardness. Under a load of 100 g ($P = 0.1 \text{ kgf}$), a brass-yellow mineral gives an indentation with mean diagonal $30 \mu\text{m}$ ($d = 0.030 \text{ mm}$):

$$\text{VHN} = \frac{1.8544 \times 0.1}{(0.030)^2} = \frac{0.18544}{0.0009} \approx 206 \text{ kg/mm}^2$$

This is in the range of chalcopyrite (about 180–220), and far below pyrite (about 1,500), the other common yellow sulphide.

Other properties include crystal form and habit (euhedral pyrite cubes and arsenopyrite rhombs; bladed hematite; tabular molybdenite), cleavage (triangular cleavage pits in galena), twinning (lamellar twins in hematite and ilmenite, cyclic twins in cassiterite), magnetism (magnetite and pyrrhotite attract a magnetised needle) and the behaviour of tarnish.

Mineral	Formula	Colour in reflected light (air)	R (%)	Anisotropy	VHN	Other features
Pyrite	FeS_2	Pale yellowish white	54	Isotropic	1,500	Cubes; brittle
Marcasite	FeS_2	Creamy white	49–55	Strong	1,000	Spear shapes
Arsenopyrite	FeAsS	White	51	Moderate	1,100	Rhombs; may host gold

Mineral	Formula	Colour in reflected light (air)	R (%)	Anisotropy	VHN	Other features
Chalcopyrite	CuFeS ₂	Brass yellow	44	Weak	200	Softer than pyrite
Pyrrhotite	Fe _{1-x} S	Creamy pinkish brown	38–40	Strong	230–320	Magnetic
Galena	PbS	White	43	Isotropic	70–80	Triangular pits
Sphalerite	ZnS	Grey	16–17	Isotropic	190–210	Yellow-brown int. refl.
Bornite	Cu ₅ FeS ₄	Pinkish brown, tarnishes purple	22	Very weak	90	With chalcopyrite
Chalcocite	Cu ₂ S	Bluish grey white	32	Weak	80	Supergene rims
Covellite	CuS	Deep blue to bluish white	7–22	Extreme (orange)	100	Pleochroic
Magnetite	Fe ₃ O ₄	Grey with brownish tint	20–21	Isotropic	530–600	Magnetic
Hematite	Fe ₂ O ₃	Grey-white with bluish tint	26–30	Distinct	1,000	Red int. refl.
Ilmenite	FeTiO ₃	Brownish grey	17–21	Strong	600	Lamellae in magnetite
Cassiterite	SnO ₂	Grey	11–13	Weak to moderate	1,000	Brown int. refl.; twins
Columbite	(Fe,Mn)Nb ₂ O ₆	Grey	16–17	Weak	650	Red-brown int. refl.
Native gold	Au	Bright yellow	70+	Isotropic	50	Very soft
Molybdenite	MoS ₂	Grey-white	15–37	Extreme	20	Bent flakes

Values are approximate and vary with composition and wavelength (after Craig and Vaughan, 1994; Pracejus, 2015). "Int. refl." = internal reflections.

3.4 A scheme for identifying ore minerals

Identification combines several properties, used in order from the quickest to the most specific (Figure 3.3):

1. Note the **colour** in PPL compared with neighbouring minerals: is the mineral distinctly coloured (yellow, blue, pink, brown) or white to grey?
2. Estimate the **reflectance**: is it brighter or darker than known minerals such as pyrite, galena, magnetite or sphalerite?
3. Cross the polars and rotate the stage: is the mineral **isotropic or anisotropic**, and does it show **internal reflections**?
4. Compare **polishing hardness** with neighbouring minerals, and look at **crystal form**, cleavage and twinning.

5. If needed, confirm with quantitative measurements of reflectance and VHN, or with chemical analysis by SEM-EDS or EPMA (Section 1).

Two common pitfalls are worth remembering. First, pyrite, chalcopyrite and gold are all yellow, but they differ in reflectance, hardness and shade: pyrite is pale and very hard, chalcopyrite brass yellow and much softer, gold bright yellow and very soft. Second, sphalerite, magnetite and cassiterite are all grey and isotropic or weakly anisotropic; sphalerite and cassiterite show abundant internal reflections, while magnetite shows none and is magnetic.

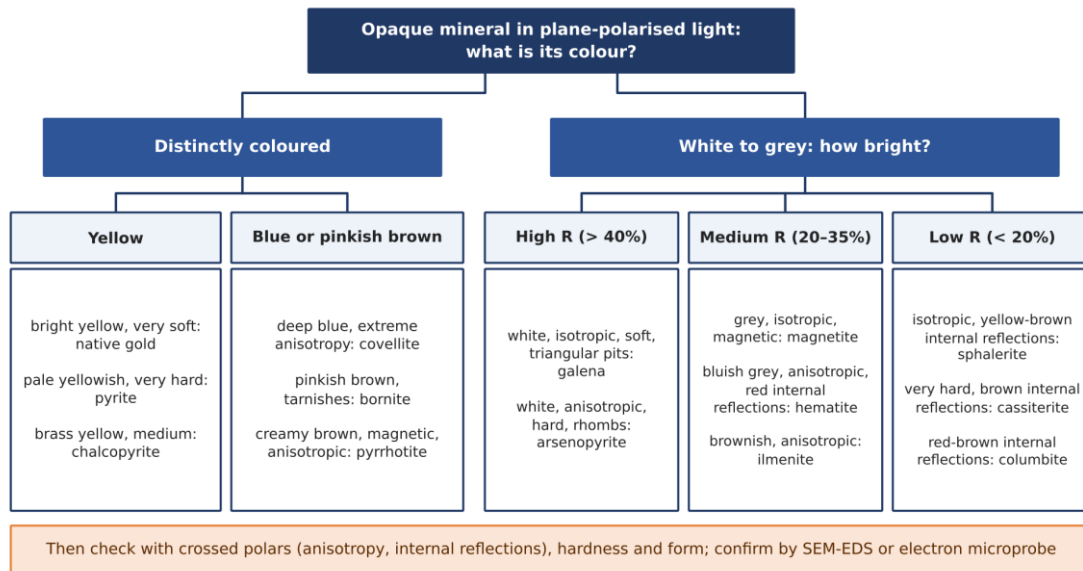


Figure 3.3. A simplified scheme for identifying common ore minerals in reflected light, using colour, reflectance, anisotropy and internal reflections. Final confirmation is by SEM-EDS or electron microprobe.

3.5 Ore textures

Textures are the shapes, sizes and arrangements of mineral grains and their mutual relationships. They record how the ore formed and what happened to it afterwards. Figure 3.4 shows six common types.

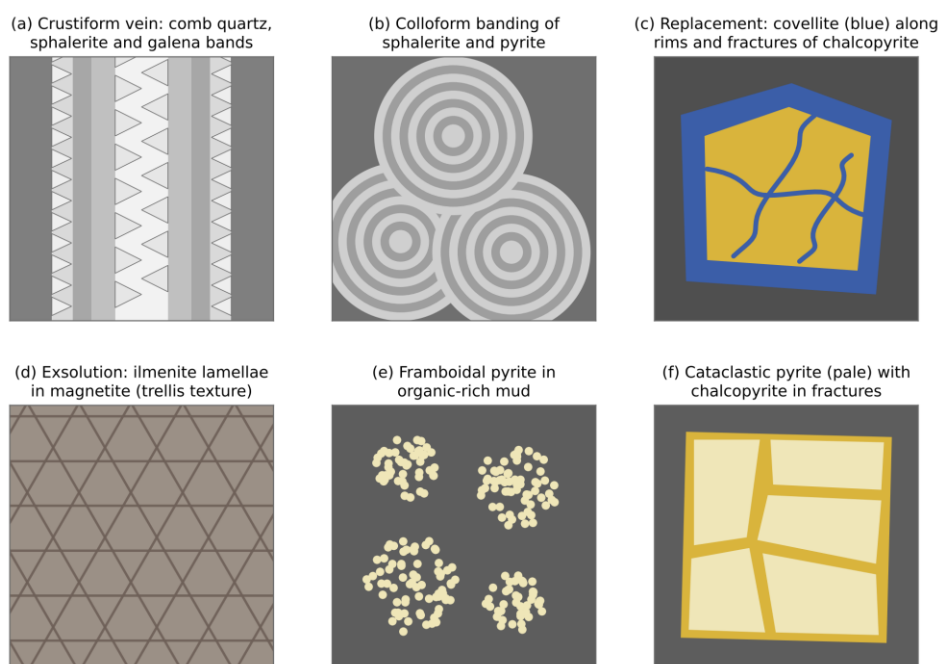


Figure 3.4. Common ore textures in reflected light (sketches): (a) open-space filling with crustiform bands; (b) colloform banding; (c) replacement of chalcopyrite by covellite along rims and fractures; (d) exsolution lamellae of ilmenite in magnetite; (e) framboidal pyrite; (f) cataclastic pyrite with fractures filled by chalcopyrite.

Open-space filling. Minerals that grew into open fractures and cavities form crystals with well-developed faces pointing into the open space (comb texture), symmetrical layers on both walls of a vein (**crustiform banding**), concentric layers around fragments (cockade texture) and vugs. These textures are typical of epithermal and other veins formed at shallow depth.

Colloform textures. Fine, rounded, concentric bands of sphalerite, pyrite, marcasite or iron oxides form by rapid precipitation from supersaturated fluids, possibly from colloidal gels. They are common in seafloor sulphide chimneys, Mississippi Valley-type deposits and in supergene alteration.

Replacement textures. One mineral may be replaced by another, often preserving the shape of the original. Replacement typically starts at grain boundaries, cleavages and fractures, producing rims, veinlets and island-like relics of the earlier mineral (**caries** or **atoll textures**). Examples include the replacement of chalcopyrite by covellite and chalcocite during supergene enrichment, of magnetite by hematite (**martite**) during oxidation, and of pyrrhotite by pyrite and marcasite. **Pseudomorphs**, such as goethite after pyrite, preserve the crystal form of the replaced mineral.

Exsolution textures. A solid solution that is stable at high temperature may separate on cooling into two minerals, producing oriented lamellae, blebs or flames of one mineral within another. Examples include lamellae of ilmenite in magnetite (often formed by oxidation during cooling), hematite-ilmenite intergrowths, flames of pentlandite in pyrrhotite in magmatic nickel ores, and lamellae of chalcopyrite in bornite. Because exsolution depends on temperature, such textures give clues to the cooling history of the ore. The fine “chalcopyrite disease” of sphalerite, in contrast, mostly forms by replacement or co-precipitation rather than true exsolution.

Sedimentary and diagenetic textures. Framboids of pyrite (Section 2.7), detrital grains of gold, cassiterite and ilmenite in placers, and oolitic iron ores reflect formation in sediments.

Deformation and metamorphic textures. Brittle minerals such as pyrite and arsenopyrite fracture under stress (**cataclastic texture**), and the fractures are filled by softer, more mobile

minerals such as chalcopyrite and galena. Soft minerals deform plastically: galena shows curved cleavage traces with bent rows of triangular pits. During metamorphism, sulphides recrystallise into polygonal grains meeting at triple junctions of about 120° (**annealing** or foam texture), and pyrite may grow into large porphyroblasts.

3.6 Paragenesis

The **paragenesis** of a deposit is the sequence in which its minerals formed. It is worked out from textural criteria, such as:

- a vein or veinlet is younger than the minerals it cuts;
- a replacing mineral is younger than the mineral it replaces;
- a mineral with crystal faces against another usually formed earlier, and the later mineral filled the space around it;
- inclusions are usually, but not always, older than their host;
- exsolution products form at the same time as, or after, their host.

The results are summarised in a **paragenetic diagram**, in which the minerals are listed and their periods of formation are shown as bars against a relative time scale divided into stages (Figure 3.5). The paragenesis helps to show how the ore-forming fluids changed, for example from early hot, iron-rich fluids that deposited pyrite to later, cooler fluids that deposited sphalerite and galena, and how supergene weathering modified the ore near the surface.

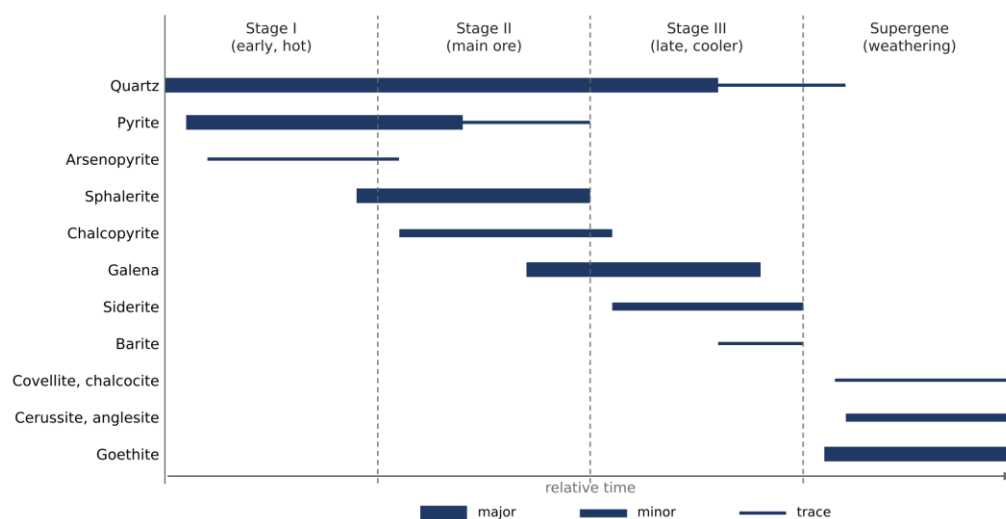


Figure 3.5. A paragenetic diagram for a hypothetical hydrothermal lead-zinc-copper vein. Bars show the relative periods of crystallisation of each mineral in successive stages; line thickness indicates relative abundance.

3.7 Applied ore mineralogy

Modal analysis by point counting. The proportion of each mineral in a polished section can be estimated by counting the mineral under the cross-hairs at a large number N of points on a regular grid, or by image analysis. The volume percentage of mineral i counted at n_i points is

$$V_i = 100 \times \frac{n_i}{N}$$

and its approximate standard error is

$$\sigma_i = \sqrt{\frac{V_i (100 - V_i)}{N}}$$

Volume percentages are converted to weight percentages using the densities ρ of the minerals:

$$w_i = 100 \times \frac{V_i \rho_i}{\sum_j V_j \rho_j}$$

Worked example: copper grade from a point count. In a polished section of copper ore, 500 points are counted: 40 on chalcopyrite ($\rho = 4.19 \text{ g/cm}^3$), 60 on pyrite ($\rho = 5.01$) and 400 on quartz ($\rho = 2.65$). The volume percentages are 8.0%, 12.0% and 80.0%, and the standard error for chalcopyrite is $\sqrt{8 \times 92/500} \approx 1.2\%$. The weight percentages are

$$w_{\text{cpy}} = 100 \times \frac{8.0 \times 4.19}{8.0 \times 4.19 + 12.0 \times 5.01 + 80.0 \times 2.65} = 100 \times \frac{33.5}{305.7} \approx 11.0\%$$

and similarly pyrite 19.7% and quartz 69.4%. Chalcopyrite contains 34.6 wt% Cu, so the copper grade is about $11.0 \times 0.346 \approx 3.8\%$ Cu. In practice, many sections must be counted to obtain a representative grade.

Grain size and liberation. For a mineral to be recovered by flotation, gravity or magnetic separation, it must be freed, or **liberated**, from the gangue by crushing and grinding. The required grind size depends on the grain size and intergrowths of the valuable minerals seen under the microscope. Coarse, simple intergrowths are liberated by coarse grinding; fine, complex intergrowths, such as fine chalcopyrite in sphalerite, require fine grinding and are hard to separate cleanly. Automated SEM-based mineralogy (Section 1.6) now measures liberation on thousands of particles, and the combination of mineralogy with metallurgical testing is called **geometallurgy**.

Problem minerals. Ore microscopy identifies minerals that affect processing or the environment. Gold locked as submicroscopic particles in arsenopyrite or pyrite is **refractory**, and cannot be extracted by simple cyanide leaching without roasting or pressure oxidation. Arsenopyrite releases arsenic, and pyrite and pyrrhotite generate acid mine drainage. Graphite and carbonaceous matter adsorb dissolved gold (“preg-robbing”), and clay minerals interfere with flotation and thickening.

Examples in Nigeria. Ore mineralogy is applied to all of Nigeria’s main metallic resources:

- the **cassiterite** and **columbite** of the tin fields of the Jos Plateau, derived from the Younger Granites and concentrated in alluvial placers; the two minerals look alike in hand specimen but differ in reflected light (columbite has red-brown internal reflections) and are separated by their different magnetic properties;
- the **galena** and **sphalerite**, with chalcopyrite, of the lead–zinc veins of the Benue Trough;
- the **gold** of the schist belts of the north-west and south-west, where the relationships of gold to quartz, pyrite and arsenopyrite control its recovery;
- the **ilmenite**, **rutile**, **zircon** and other heavy minerals of beach and offshore placer sands, of direct interest to marine geologists, whose grain size, alteration (such as ilmenite altering to leucoxene) and intergrowths determine their value.

3.8 Key points of Section 3

- Opaque ore minerals are studied in reflected light on polished sections with the ore microscope, in plane-polarised light and with crossed polars.

- The key properties are colour, reflectance, bireflectance, anisotropy, internal reflections and hardness; reflectance follows the Fresnel equation and Vickers hardness is $1.8544P/d^2$.
- Minerals are identified systematically, with confirmation by SEM-EDS or EPMA where needed.
- Textures of open-space filling, colloform growth, replacement, exsolution, sedimentation and deformation record the origin and history of an ore; paragenesis is the sequence of mineral formation.
- Point counting gives modal mineralogy and grade; grain size, intergrowths and problem minerals determine how an ore is processed.

Summary, review questions and glossary

Summary

Topic	Main ideas
X-rays and XRD	Continuous and characteristic X-rays; Moseley's law; Bragg's law; d-spacings and unit cells; powder diffractometer; identification, quantification and crystallite size
Electron beam methods	Interaction volume; secondary and backscattered electrons; EDS and WDS; electron microprobe, standards and ZAF corrections; mineral formula calculation
Bulk and other methods	XRF on fused beads and pellets; ICP-MS and LA-ICP-MS; Raman, FTIR, thermal analysis, Mössbauer, automated mineralogy
Clay minerals	Tetrahedral and octahedral sheets; 1:1 and 2:1 layers; layer charge; kaolinite, illite, smectite, vermiculite, chlorite; CEC and swelling; XRD of oriented mounts with glycol and heat treatments
Clays and authigenic minerals in the sea	Detrital clay distribution and climate; smectite-to-illite diagenesis; glauconite, verdine, phosphorite, zeolites, pyrite, evaporites, barite, Fe-Mn oxides; industrial clays
Ore mineralogy	Ore microscope and polished sections; colour, reflectance, anisotropy, internal reflections, hardness; identification scheme; textures; paragenesis; point counting, grade, liberation and problem minerals

Summary of key equations

Quantity	Equation	Section
Photon energy and wavelength	$E \text{ (keV)} \approx 12.398/\lambda \text{ (Å)}$	1.2
Moseley's law ($K\alpha$ lines)	$E_{K\alpha} \approx 10.2 \text{ eV} \times (Z - 1)^2$	1.2
Bragg's law	$n\lambda = 2d\sin\theta$	1.3
Cubic d-spacing	$1/d^2 = (h^2 + k^2 + l^2)/a^2$	1.3
Hexagonal d-spacing	$1/d^2 = 4/3 (h^2 + hk + k^2)/a^2 + l^2/c^2$	1.3
Scherrer equation	$\tau = K\lambda/(\beta\cos\theta)$	1.3
Kanaya-Okayama range	$R = 0.0276 A E_0^{1.67} / (Z^{0.89} \rho)$	1.4

Quantity	Equation	Section
Forsterite content	$Fo = 100 \text{ Mg}/(\text{Mg} + \text{Fe})$	1.5
Cation exchange capacity	$CEC = (x/M) \times 10^5 \text{ meq}/100 \text{ g}$	2.4
Fresnel reflectance	$R = [(n - N)^2 + k^2]/[(n + N)^2 + k^2]$	3.3
Vickers hardness	$VHN = 1.8544 P/d^2$	3.3
Point-count volume % and error	$V_i = 100 n_i/N; \sigma_i = \sqrt{V_i(100 - V_i)/N}$	3.7
Volume to weight %	$w_i = 100 V_i \rho_i / \sum_j V_j \rho_j$	3.7

Review questions

Part A: Short answers

1. Explain how continuous and characteristic X-rays are produced in an X-ray tube.
2. State Bragg's law and explain each term with a labelled diagram.
3. Why is a powder used for X-ray diffraction of minerals? What information is obtained from the positions, intensities and widths of the peaks?
4. Why is it difficult to detect amorphous materials and minor minerals by XRD?
5. Describe the signals produced when an electron beam strikes a sample and state what each is used for.
6. Why do galena and zircon appear bright, and quartz dark, in a backscattered electron image?
7. Compare EDS and WDS in terms of speed, energy resolution and detection limit.
8. What are ZAF corrections, and why are they needed in electron microprobe analysis?
9. Why are electron microprobe analyses of micas and amphiboles less than 100%?
10. Distinguish between dioctahedral and trioctahedral sheets, and between 1:1 and 2:1 layers.
11. Explain why smectite swells but illite does not.
12. Describe the treatments used to identify clay minerals by XRD and the response of each clay group.
13. How would you distinguish kaolinite from chlorite in a clay sample?
14. Explain why kaolinite is abundant in deep-sea sediments of the tropics and chlorite at high latitudes.
15. Describe the conditions in which glauconite forms and explain its importance in sequence stratigraphy.
16. How do acid sulphate soils develop in mangrove areas?
17. What is an internal reflection? Name three minerals that show distinctive internal reflections.
18. How would you distinguish pyrite, chalcopyrite and native gold in reflected light?

Part B: Calculations

19. Using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), calculate the d-spacing for a peak at $2\theta = 29.41^\circ$. Which common mineral does it suggest?

20. Galena is cubic with $a = 5.936 \text{ \AA}$. Calculate the d-spacing and the 2θ angle (Cu $K\alpha$) of its (200) reflection.
21. A clay peak at $2\theta = 12.35^\circ$ has a width (after correction) of 0.40° . Estimate the crystallite size with the Scherrer equation ($K = 0.9$).
22. Estimate the depth of the interaction volume in iron ($A = 55.85$, $Z = 26$, $\rho = 7.87 \text{ g/cm}^3$) at 20 keV, and compare it with that in silicon at 15 keV.
23. An olivine gives SiO_2 38.5, FeO 23.0, MnO 0.3 and MgO 38.3 wt%. Calculate its formula on the basis of 4 oxygens and its forsterite content.
24. A smectite has a layer charge of 0.5 per $\text{O}_{10}(\text{OH})_2$ and a formula weight of 370 g/mol. Estimate its CEC.
25. A Vickers indentation made with a 100 g load has a mean diagonal of $11 \text{ }\mu\text{m}$. Calculate the VHN and suggest which common sulphide it could be.
26. A point count of 400 points on a lead–zinc ore gives 25 points on galena ($\rho = 7.58$), 50 on sphalerite ($\rho = 4.05$) and 325 on quartz ($\rho = 2.65$). Calculate the volume and weight percentages and the Pb and Zn grades.

Part C: Essays

27. Describe how you would identify and characterise the minerals in a sample of marine mud from the Niger Delta shelf, from sample preparation to the final report.
28. Compare the uses of XRD, SEM-EDS, EPMA and XRF in the study of a heavy mineral sand deposit.
29. Discuss the origin and significance of authigenic minerals in marine sediments.
30. Explain how ore mineralogy contributes to the exploration, mining and processing of an ore deposit, with examples from Nigeria.

Glossary

Term	Meanin
Anisotropic	Showing changes in brightness or colour on rotation under crossed polars
Authigenic	Formed in place, in the sediment or water column
Backscattered electrons	Beam electrons scattered back out of a sample; their yield increases with atomic number
Basal spacing	The repeat distance d_{001} between successive layers of a clay mineral
Bragg's law	$n\lambda = 2d\sin\theta$, the condition for diffraction from lattice planes
Cation exchange capacity	The amount of exchangeable cations a clay can hold, in meq/100 g
Characteristic X-rays	X-rays of fixed energy emitted when inner-shell vacancies are filled
Diocahedral	Octahedral sheet with two of every three sites occupied, mainly by Al^{3+}
EDS	Energy-dispersive spectrometry: all X-ray energies measured at once
EPMA	Electron probe microanalyser, used for accurate quantitative analysis of grains
Exsolution	Separation of a solid solution into two minerals on cooling
Glauconite	Green, K– Fe^{3+} -rich 2:1 clay forming as pellets on the outer shelf

Term	Meanin
Internal reflections	Light reflected back from within a partly transparent mineral
Layer charge	The net negative charge of a 2:1 clay layer per $O_{10}(OH)_2$
Liberation	The freeing of valuable mineral grains from gangue by crushing and grinding
Paragenesis	The sequence in which the minerals of a deposit formed
Phosphorite	Sedimentary rock rich in carbonate fluorapatite
Reflectance	Percentage of incident light reflected from a polished surface
Trioctahedral	Octahedral sheet with all three sites occupied, mainly by Mg^{2+} or Fe^{2+}
VHN	Vickers hardness number, $1.8544P/d^2$ in kg/mm^2
WDS	Wavelength-dispersive spectrometry, using diffracting crystals
ZAF corrections	Corrections for atomic number, absorption and fluorescence in microanalysis

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