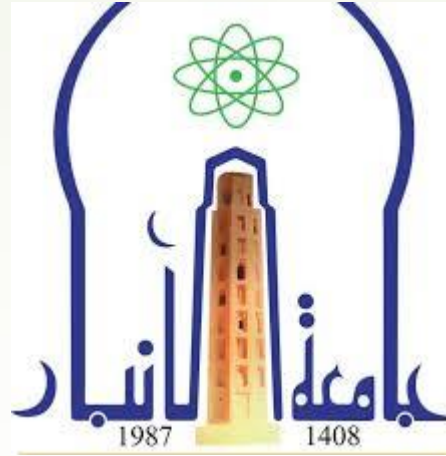


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Carbonate, Sulfate and Phosphate Minerals Groups

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**CARBONATE, SULFATE AND
PHOSPHATE MINERALS
GROUPS**

LECTURE SEVEN

CARBONATE MINERAL GROUP

- The carbonate minerals contain the anionic complex CO_3^{2-} , which is triangular in its coordination—i.e., with a carbon atom at the center and an oxygen atom at each of the corners of an equilateral triangle. These anionic groups are strongly bonded individual units and do not share oxygen atoms with one another. The triangular carbonate groups are the basic building units of all carbonate minerals and are largely responsible for the properties particular to the class.
- The common anhydrous (water-free) carbonates are divided into three groups that differ in structure type: calcite, aragonite, and dolomite.
- The copper carbonates azurite and malachite are the only notable hydrous varieties.

- This anion group usually occurs in combination with calcium, sodium, uranium, iron, aluminum, manganese, barium, zinc, copper, lead, or the rare-earth elements. The carbonates tend to be soft, soluble in hydrochloric acid, and have a marked anisotropy in many physical properties (e.g., high birefringence) as a result of the planar structure of the carbonate ion.

- There are approximately 80 known carbonate minerals, but most of them are rare. The commonest varieties, **calcite, dolomite, and aragonite**, are prominent constituents of certain rocks: calcite is the principal mineral of limestone's and marbles; dolomite occurs as a replacement for calcite in limestone's, and when this is extensive the rock is termed dolomite; and aragonite occurs in some recent sediments and in the shells of organisms that have calcareous skeletons. **Other relatively common carbonate minerals serve as metal ores: siderite, for iron; rhodochrosite, for manganese; strontianite, for strontium; smithsonite, for zinc; witherite, for barium; and cerussite, for lead.**

- Most such rock-forming carbonates belong to one of two structure groups—either calcite or aragonite. The calcite structure is usually described with reference to the sodium chloride structure in which the sodium and chloride of halite are replaced by calcium atoms and CO₃ groups, respectively. The unit cell of halite is distorted by compression along a three-fold axis, resulting in a rhombohedral cell. In calcite all CO₃ groups are parallel and lie in horizontal layers; CO₃ groups in adjacent layers, however, point in opposite directions. The calcium atoms are bonded to six oxygen atoms, one each from three CO₃ groups in a layer above and three from CO₃ groups in a layer below.

- The structure of dolomite, $\text{CaMg}(\text{CO}_3)_2$, is similar to that of calcite, CaCO_3 , except that there is regular alternation of calcium and magnesium, and a lower symmetry, though still rhombohedral, results. The composition CaCO_3 most commonly occurs in two different polymorphs: **rhombohedral** calcite with calcium surrounded by six closest oxygen atoms and **orthorhombic** aragonite with calcium surrounded by nine closest oxygen atoms.
- **Natural occurrence**
- Calcite is a common constituent of sedimentary rocks, limestone in particular, much of which is formed from the shells of dead marine organisms. Approximately 10% of sedimentary rock is limestone. It is the primary mineral in metamorphic marble. It also occurs in deposits from hot springs as a vein mineral; in caverns as stalactites and stalagmites; and in volcanic or mantle-derived rocks such as carbonatites, kimberlites, or rarely in peridotites.

Physical Properties of Calcite

Chemical Classification	Carbonate
Color	Usually white but also colorless, gray, red, green, blue, yellow, brown, orange
Streak	White
Luster	Vitreous
Diaphaneity	Transparent to translucent
Cleavage	Perfect, rhombohedral, three directions
Mohs Hardness	3
Specific Gravity	2.7
Diagnostic Properties	Rhombohedral cleavage, powdered form effervesces weakly in dilute HCl, curved crystal faces and frequent twinning
Chemical Composition	CaCO₃
Crystal System	Hexagonal
Uses	Acid neutralization, a low-hardness abrasive, soil conditioner, heated for the production of lime



Physical Properties of Dolomite

Chemical Classification	Carbonate
Color	Colorless, white, pink, green, gray, brown, black
Streak	White
Luster	Vitreous, pearly
Diaphaneity	Transparent to translucent
Cleavage	Perfect, rhombohedral, three directions
Mohs Hardness	3.5 to 4
Specific Gravity	2.8 to 2.9
Diagnostic Properties	Rhombohedral cleavage, powdered form effervesces weakly in dilute HCl, hardness
Chemical Composition	$\text{CaMg}(\text{CO}_3)_2$
Crystal System	Hexagonal
Uses	Construction aggregate, cement manufacture, dimension stone, calcined to produce lime, sometimes an oil and gas reservoir, a source of magnesia for the chemical industry, agricultural soil treatments, metallurgical flux



<u>Category</u>	<u>Carbonate mineral</u>
<u>Formula</u> (repeating unit)	CaCO_3
<u>Crystal system</u>	<u>Orthorhombic</u>
<u>Color</u>	<i>White, red, yellow, orange, green, purple, grey, blue and brown</i>
<u>Cleavage</u>	<i>Distinct on {010}, imperfect {110} and {011}</i>
<u>Fracture</u>	<i>Subconchoidal</i>
<u>Tenacity</u>	<i>Brittle</i>
<u>Mohs scale hardness</u>	<i>3-5</i>
<u>Luster</u>	<i>Vitreous, resinous on fracture surfaces</i>
<u>Streak</u>	<i>White</i>
<u>Diaphaneity</u>	<i>Translucent to transparent</i>
<u>Specific gravity</u>	<i>2.90</i>



SULFATES

- This class is composed of a large number of minerals, but relatively few are common. All contain anionic $(\text{SO}_4)^{2-}$ groups in their structures. i.e., ions in which four oxygen atoms are symmetrically distributed at the corners of a tetrahedron with the sulfur atom in the center. These anionic complexes are formed through the tight bonding of a central S^{6+} ion_ to four neighboring [oxygen](#) atoms in a tetrahedral arrangement around the sulfur. This closely knit group is incapable of sharing any of its oxygen atoms with other SO_4 groups; as such, the tetrahedrons occur as individual, unlinked groups in [sulfate mineral](#) structures.

- sulfate also spelled Sulphate, any naturally occurring salt of sulfuric acid. About 200 distinct kinds of sulfates are recorded in mineralogical literature, but most of them are of rare and local occurrence. Abundant deposits of sulfate minerals, such as barite and celestite, are exploited for the preparation of metal salts. Many beds of sulfate minerals are mined for fertilizer and salt preparations, and beds of pure gypsum are mined for the preparation of plaster of paris.
- Sulfate minerals can be found in at least four kinds: as late oxidation products of preexisting sulfide ores, as evaporite deposits, in circulatory solutions, and in deposits formed by hot water or volcanic gases

- . Many sulfate minerals occur as basic hydrates of iron, cobalt, nickel, zinc, and copper at or near the source of preexisting primary sulfides. The sulfide minerals, through exposure to weathering and circulating water, have undergone oxidation in which the sulfide ion is converted to sulfate and the metal ion also is changed to some higher valence state. Noteworthy beds of such oxidation products occur in desert regions, where brightly coloured basic copper and ferric iron sulfates have accumulated. The sulfate anions generated by oxidation processes may also react with calcium carbonate rocks to form gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Sulfates formed by the oxidation of primary sulfides include antlerite $[\text{Cu}_3(\text{SO}_4)(\text{OH})_4]$, brochantite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6]$, chalcantite $[\text{Cu}^{2+}(\text{SO}_4) \cdot 5\text{H}_2\text{O}]$, anglesite (PbSO_4) , and plumbojarosite $[\text{PbFe}^{3+}_6(\text{SO}_4)_4(\text{OH})_{12}]$.

- Soluble alkali and alkaline–earth sulfates crystallize upon evaporation of sulfate–rich brines and trapped oceanic salt solutions. Such brines can form economically important deposits of sulfate, halide, and borate minerals in thick parallel beds, as the potash deposits at Stassfurt, Ger., and the southwestern United States. Many of the sulfate minerals are salts of more than one metal, such as polyhalite, which is a combination of potassium, calcium, and magnesium sulfates.
- Sulfate minerals common in evaporite deposits include anhydrite, **gypsum**, thenardite (Na_2SO_4), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), glauberite [$\text{Na}_2\text{Ca}(\text{SO}_4)_2$], kainite ($\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and polyhalite [$\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$].

- Groundwater carrying sulfate anions reacts with calcium ions in muds, clays, and limestones to form beds of gypsum. The massive material is called alabaster or plaster of paris (originally found in the clays and muds of the Paris basin). If such beds become deeply buried or metamorphosed (altered by heat and pressure), anhydrite may form by dehydration of the gypsum.
- Numerous sulfates, usually simple, are formed directly from hot aqueous solutions associated with fumarolic (volcanic gas) vents and late-stage fissure systems in ore deposits. Noteworthy examples include anhydrite, barite, and celestine.

Physical Properties of Gypsum

<i>Chemical Classification</i>	<i>Sulfate</i>
<i>Color</i>	<i>Clear, colorless, white, gray, yellow, red, brown</i>
<i>Streak</i>	<i>White</i>
<i>Luster</i>	<i>Vitreous, silky, sugary</i>
<i>Diaphaneity</i>	<i>Transparent to translucent</i>
<i>Cleavage</i>	<i>Perfect</i>
<i>Mohs Hardness</i>	<i>2</i>
<i>Specific Gravity</i>	<i>2.3</i>
<i>Diagnostic Properties</i>	<i>Cleavage, specific gravity, low hardness</i>
<i>Chemical Composition</i>	<i>Hydrous calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$</i>
<i>Crystal System</i>	<i>Monoclinic</i>
<i>Uses</i>	<i>Used to manufacture dry wall, plaster, joint compound. An agricultural soil treatment.</i>



Physical Properties of Anhydrite

Chemical Classification Sulfate

<i>Color</i>	<i>Colorless, white, and light shades of brown, red, gray, pink, blue, violet</i>
<i>Streak</i>	<i>White</i>
<i>Luster</i>	<i>Vitreous to pearly</i>
<i>Diaphaneity</i>	<i>Transparent to translucent</i>
<i>Cleavage</i>	<i>Perfect cleavage in three directions to form cubic-shaped cleavage fragments</i>
<i>Mohs Hardness</i>	<i>3 to 3.5</i>
<i>Specific Gravity</i>	<i>2.9 to 3</i>
<i>Diagnostic Properties</i>	<i>Cubic cleavage, harder than gypsum, higher specific gravity than calcite, no acid reaction.</i>
<i>Chemical Composition</i>	<i>CaSO_4</i>
<i>Crystal System</i>	<i>Orthorhombic</i>
<i>Uses</i>	<i>Soil treatment. Ingredient in plaster and other construction materials.</i>



Physical Properties of Barite

Chemical Classification

Sulfate

Color

Colorless, white, light blue, light yellow, light red, light green

Streak

White

Luster

Vitreous to pearly

Diaphaneity

Transparent to translucent

Cleavage

Very good, basal, prismatic

Mohs Hardness

2.5 to 3.5

Specific Gravity

4.5

Diagnostic Properties

High specific gravity, three cleavage directions at right angles

Chemical Composition

Barium sulfate, $BaSO_4$

Crystal System

Orthorhombic

Uses

Drilling mud; high-density filler for paper, rubber, plastics



PHOSPHATE MINERAL

Phosphate mineral, any of a group of naturally occurring inorganic salts of phosphoric acid, $H_3(PO_4)$. More than 200 species of phosphate minerals are recognized, and structurally they all have isolated (PO_4) tetrahedral units. Phosphates can be grouped as: (1) primary phosphates that have crystallized from a liquid; (2) secondary phosphates formed by the alteration of primary phosphates; and (3) fine-grained rock phosphates formed at low temperatures from phosphorus-bearing organic material, primarily underwater.

1-Primary phosphates usually crystallize from aqueous fluids derived from the late stages of crystallization. Particularly common in granitic pegmatites are the primary phosphates apatite $[\text{Ca}_5(\text{F,Cl,OH})(\text{PO}_4)_3]$, triphylite $[\text{LiFePO}_4]$, lithiophilite $[\text{LiMnPO}_4]$, and the rare-earth phosphates monazite $[(\text{LaCe})(\text{PO}_4)]$ and xenotime $[\text{Y}(\text{PO}_4)]$. Primary phosphates commonly occur in ultramafic rocks (i.e., those very low in silica), including carbonatites and nepheline syenites. Metamorphic apatite occurs in calc-silicate rocks and impure limestones.

2-Secondary phosphates are extremely varied, forming at low temperatures, in the presence of water, and under variable oxidation states. Both di- and tri-valent oxidation states of iron and manganese are usually present, producing brilliant colors. Two common species are strengite $[\text{Fe}(\text{PO}_4)(\text{H}_2\text{O})_2]$ and vivianite $[\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_8]$.

Physical Properties of Apatite

Chemical Classification	Phosphate
Color	Green, brown, blue, yellow, violet, pink, colorless. Transparent specimens with excellent clarity and vivid color are used as gemstones.
Streak	White
Luster	Vitreous to subresinous
Diaphaneity	Transparent to translucent
Cleavage	Poor to indistinct
Mohs Hardness	5
Specific Gravity	3.1 to 3.3
Diagnostic Properties	Color, crystal form, and hardness. Brittle, often highly fractured. Can be scratched with a steel knife blade.
Chemical Composition	A group of calcium phosphates. Fluorapatite: $\text{Ca}_5(\text{PO}_4)_3\text{F}$ Hydroxylapatite: $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ Chlorapatite: $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ Carbonate-rich apatite/francolite: $\text{Ca}_5(\text{PO}_4\text{CO}_3)_3(\text{F},\text{O})$
Crystal System	Hexagonal
Uses	Fertilizer, phosphoric acid, hydrofluoric acid, gemstones, ore of rare earth elements, pigments, gemstone. Serves as a hardness of 5 on the Mohs Hardness Scale.



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