Crystallography
for Geology and
Chemistry Students

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This course is intended to the students of:

1. The first year (Geology) and,
2. The second year (Physics and Chemistry).

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Preface

Minerals that are grown at favorable formation conditions occur in definite and characteristic geometrical forms known as crystals. The study of these bodies and the laws which govern their growth, shape, and geometric character is called crystallography. Although crystallography was developed as a branch of mineralogy, it has now become a separate science in itself.

Crystallography is essential to progress in the applied sciences and technology and developments in all materials areas, including metals and alloys, ceramics, glasses, and polymers, as well as drug design. It is equally vital to progress in fundamental physics and chemistry, mineralogy and geology, and computer science, and to understanding of the dynamics and processes of living systems.

Crystallography plays a huge role in our lives. This is because knowledge of crystals and their properties, and the technology that comes from them, are fundamental to electronics, and to modern living. For example, the silicon chips in electronic devices, semiconductors and microchips of many sorts, and the LCD (liquid crystal display) screen on a smart phone are all crystalline. Light emitting diodes (LEDs) are commonplace in TV screens, light bulbs, and other devices. LEDs are crystalline. Electronic clocks in devices of many sorts, microphones and telephones, pickups for guitars, and ultrasound devices in hospitals are based on the piezoelectric effect of a quartz crystal. Crystalline materials are used in photovoltaic systems to generate electricity. It is, perhaps, a stretch for mineralogists to claim credit for modern electronic devises. After all, most of the crystalline materials used in modern electronic applications today are synthetic. Yet they all have natural analogs. And, in large part, it was the study of those analogs and other investigations of mineral crystals that were the start that led to today’s industries based on crystal technology.

In the following section the elements of crystallography are presented in a brief and simple manner to introduce to the reader the more essential facts and principles of the subject.

States of Matter

Matter can be subdivided into three states-solids, fluids and gases. Although very little of the matter in the universe is in the solid state, solids constitute much of the physical world around us and a large part of the modern technology is based on the special characteristics of the various solid materials.

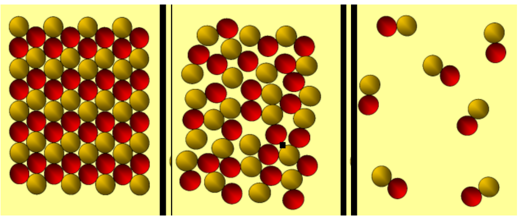


Fig. (1): The three states of matter

Based on the atomic arrangement in a substance, solids can be broadly classified as either crystalline or non-crystalline. In a crystalline solid, all the atoms are arranged in a periodic manner in all three dimensions where as in a non-crystalline solid the atomic arrangement is random or non-periodic in nature. A crystalline solid can either be a single crystalline or a polycrystalline. In the case of single crystal the entire solid consists of only one crystal and hence, periodic arrangement of atoms continues throughout the entire material. A polycrystalline material is an aggregate of many small crystals separated by well-defined grain boundaries and hence periodic arrangement of atoms is limited to small regions of the material called as grain boundaries as shown in Fig. 1.1. The non-crystalline substances are also called as amorphous substances materials. Single crystalline materials exhibit long range as well as short range periodicities while long range periodicity is absent in case of poly-crystalline materials and non-crystalline materials.

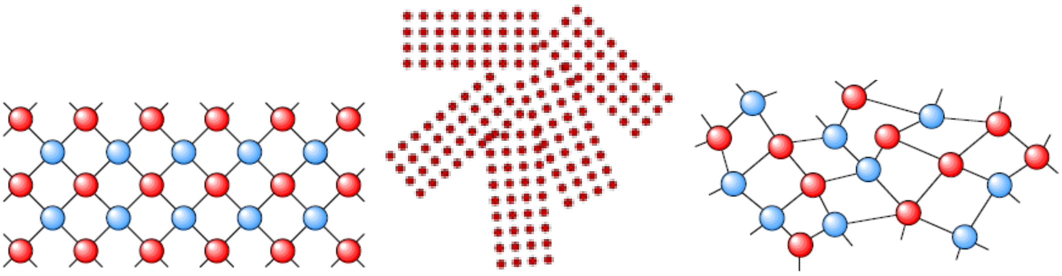


Fig. (2): Crystalline, poly-crystalline and amorphous solids

Crystallization

As it is known there are three prominent modes of crystallization. Crystals are formed from (1) solution, (2) fusion, or (3) vapor.

The first, crystallization from solution, is the most familiar to our ordinary experience. Consider, for example, a solution of sodium chloride (common salt) in water. Suppose that by evaporation the water is slowly driven off. Under these conditions the solution will gradually contain more and more salt per unit volume. Ultimately the point will be reached where the amount of water present can no longer retain all the salt in solution and the salt must begin to precipitate out. In other words, part of the sodium chloride, which up to this point has been held in a state of solution by the water, now assumes a solid form. If the conditions are so arranged that the evaporation of the water goes on very slowly, the separation of the salt in solid form will progress equally slowly and definite crystals will result. The particles of sodium chloride as they separate from the solution will by the laws of molecular attraction group themselves together and gradually build up a definitely shaped solid which we call a crystal. Crystals can also be formed from solution by lowering the temperature or pressure of the solution. Hot water will dissolve slightly more salt, for instance, than cold; and, if a hot solution is allowed to cool, a point will be reached where the solution becomes supersaturated for its temperature and salt will crystallize out. Again, the higher the pressure to which water is subjected the more salt it can hold in solution. So with the lowering of the pressure of a saturated solution supersaturation will result and crystals form. Therefore, in general, crystals may form from a solution by the evaporation of the solvent, by the lowering of the temperature, or by a decrease in pressure.

A crystal is formed from a fused mass in much the same way as from a solution. The most familiar example of crystallization from fusion is the formation of ice crystals when water freezes. Though it is not ordinarily considered in this way, water is fused ice. When the temperature is sufficiently .lowered the water can no longer remain liquid, and it becomes solid by crystallization into ice. The particles of water which were free to move in any direction in the liquid now become fixed in their position and by the laws of molecular attraction arrange themselves in a definite order to build up a solid crystalline mass. The formation of igneous rocks from molten magmas, though more complicated, is similar to the freezing of water. In the fluid magma there are many elements in a dissociated state. As the magma cools these elements gradually group themselves into different mineral molecules, which gather together and slowly crystallize to form the mineral particles of the resulting solid rock.

The third mode of crystal formation, that in which the crystals are produced from a vapor, is less common than the other two described above. The principles that underlie the crystallization are much the same. The dissociated chemical atoms, through the cooling of the gas, are brought closer together until at last they form a solid with a definite crystal structure. The most familiar example of this mode of crystallization is the formation of snowflakes: air laden with water vapor cools and snow crystals form directly from the vapor. Another example of this type of crystallization is seen in the formation of sulfur crystals about the mouths of fumaroles in volcanic regions, where crystals have been deposited from sulfur-bearing vapors.

Crystal Growth:

Natural crystals may grow wherever:

1. Their constituent atoms or ions are free to come together in the correct proportions.
2. The existing conditions are such that 'growth' will take place at a reasonably slow and steady rate.
3. The external surface of the growing crystal is not constrained (tight) physically.

Most well developed mineral crystals occur lining the walls of open spaces in rocks, such as open fractures, solution cavities and vesicles. Many such crystals have been deposited from

i) Hydrothermal solutions (hot aqueous solution)

ii) By condensation from gaseous fluids,

iii) As the result of late-stage crystallization of magma within cavities (kept open by accumulations of magmatic gases and vapors). Excellent crystals can also be grown in the laboratory by various processes such as slow cooling or evaporating of a saturated solution of a salt or by constant temperature.

In the first stage of growth, nucleation (nucleus or seed) of ions (in the solution or melt) starts – nucleus is the result of the coming together of various ions to form the initial regular structural pattern of a crystalline solid.

- A cubic crystal of NaCl, one cm along each edge, would contain approximately 10^{23} ions or atoms. The energy of attachment is greatest at corners, intermediate at edges and least in the middle faces. In some crystals, differ from NaCl – due to nonionic bonding, atoms accrete on the outer surface as clumps of atoms – outer surface develops.

Morphology of Crystals

The study of the external shape of minerals is called morphology. Shape, size and degree of development of various forms on the crystal are important.

Shape: The faces of crystals may exist in various stages of development:

Euhedral or Idiomorphic: all of the crystal faces are present,

Subhedral or Hypidiomorphic: some faces are present,

Anhedral or Xenomorphic: none of the crystal faces are developed.

On the other hand, an aggregate of anhedral crystals are called massive. They can be:

Crystalline: seen by naked eye,

Microcrystalline: seen under microscope only,

Cryptocrystalline: crystallinity of the mineral is detected only by X-rays or electron microscope, e.g., clay minerals.

Size: Mineral grain sizes are classified as:

Very coarse grained	>30 mm
Coarse grained	5-30 mm
Medium grained	1-5 mm
Fine grained	<1 mm

Crystal Parts

Crystal Faces

As crystals are formed by the repetition in three dimensions of a unit of structure, the limiting surfaces, which are known as the faces of a crystal, depend in part in the shape of the unit. They also depend on the conditions in which the crystal grows.

These conditions or external influences include temperature, pressure, nature of solution, direction of movement of the solution, and availability of open space for free growth. The resulting faces are of two kinds: like faces (have the same properties) and unlike faces (have different properties).

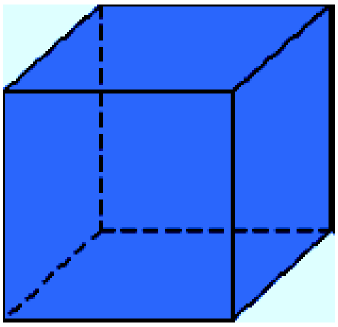


Fig. (3): Crystal Parts

Crystal Edge: An edge is formed by the intersection of any two adjacent faces.

Solid angle: A solid angle is formed by the intersection of three or more faces.

Interfacial angle: The angle between any two faces of a crystal is termed the interfacial angle.

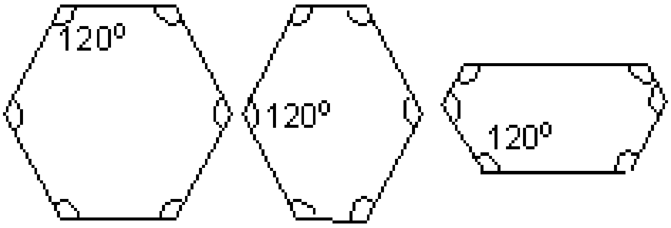


Fig. (4): Interfacial angle

An important part of the study of crystallography consists in measuring the interfacial crystal angles. These measurements are accomplished by means of instruments known as goniometers. For accurate work, particularly with small crystals, a type of instrument known as a reflection goniometer is used. This is an instrument upon which the crystal to be measured is mounted so as to reflect beams of light from its faces through a telescope to the eye. The angle through which a crystal must be turned in order to throw successive beams of light from two adjacent faces into the telescope determines the angle between the faces. A simpler instrument used for approximate work and with larger crystals is known as a contact goniometer. Its appearance and use are illustrated by Fig. 5.

Steno's Law:

Law of constancy of interfacial angles: "The angles between corresponding faces on different crystals of a substance are constant".

So, this angle was used for mineral characterization and because of its importance its measurement done by 'goniometer'.

Two types of goniometer: a) contact goniometer, b) reflecting goniometer.

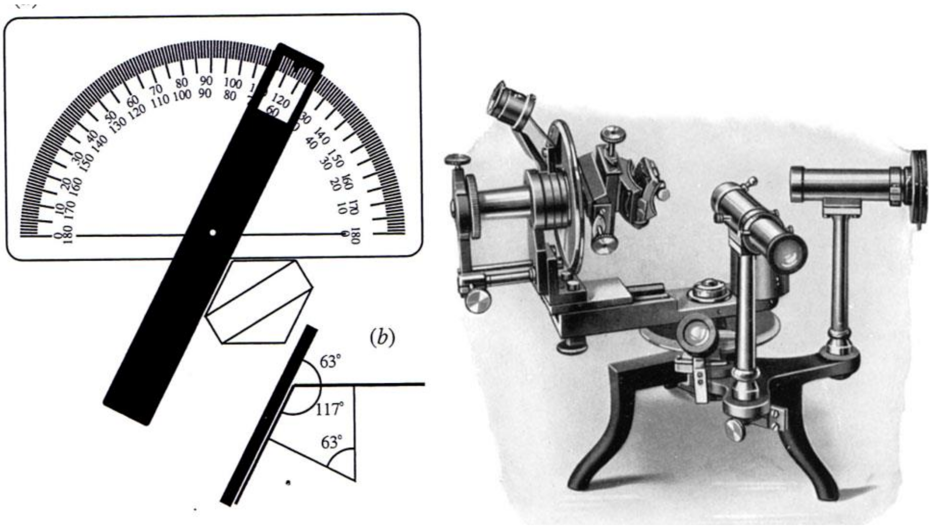


Fig. (5): a) Contact goniometer, b) reflecting goniometer.

Crystallographic Axes

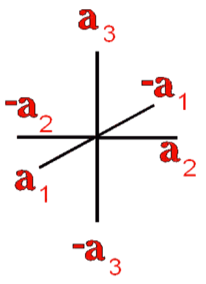
The crystallographic axes are imaginary lines that we can draw within the crystal lattice. These will define a coordinate system within the crystal. For 3-dimensional space lattices we need 3 or in some cases 4 crystallographic axes that define directions within the crystal lattices.

Depending on the symmetry of the lattice, the directions may or may not be perpendicular to one another, and the divisions along the coordinate axes may or may not be equal along the axes. As we will see later, the lengths of the axes are in some way proportional to the lattice spacing along an axis and this is defined by the smallest group of points necessary to allow for translational symmetry to reproduce the lattice.

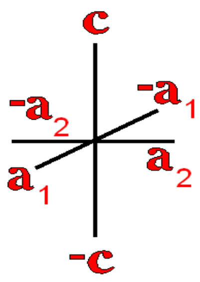
As we will see, the axes are defined based on the symmetry of the lattice and the crystal. Each crystal system has different conventions that define the orientation of the axes, and the relative lengths of the axes.

These axes aid in the orientation of crystals and help to explain other crystal concepts like unit cells and Miller Indices which we will discuss below.

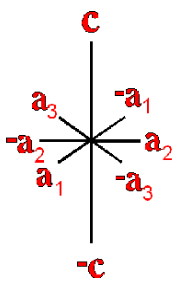
They are compared by lengths and angles of intersection with each other. They are designated as a, b and c when unequal in lengths in a crystal or by the same letter, "a" whenever equal. The "c" axis is chosen as the principal axis and can be larger or smaller than the other axes associated with it. The axes have a preferred vertical and horizontal orientation--the c axis when present always occurs in the vertical--when an a and b axis are present, they are located in the horizontal plane, the a is in a front-back orientation, and the b in a left to right position.



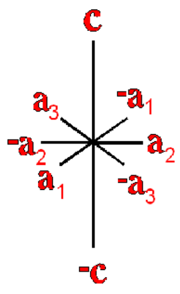
Cubic



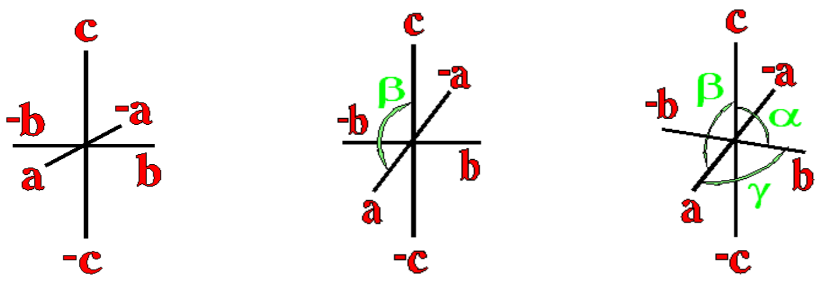
Tetragonal



Hexagonal



Trigonal



Orthorhombic Monoclinic Triclinic

Fig. (6): Crystallographic axes

In the following, we focus our discussion to crystalline solids. As already known, a crystal has regular shape and when it is broken all broken pieces have the same regular shape. A crystal has sharp melting point.

Since the crystals may have different periodic arrangements in all three dimensions, the physical properties vary with direction and therefore they are called anisotropic substances. Crystalline solids may be made up of metallic crystals or non-metallic crystals. Copper, Silver, aluminum, tungsten and magnesium are examples of metallic crystals while carbon, crystallized polymers and plastics are examples of nonmetallic crystals. Let us now discuss the elementary concepts of crystallography.

-Space Lattice or Crystal Lattice:

In a solid crystalline material, the atoms or molecules are arranged regularly and periodically in all three dimensions. The atomic arrangement in a crystal is called crystal structure. To explain crystal symmetries easily, it is convenient to represent an atom or a group of atoms that repeats in three dimensions in the crystal as a unit. If each such atom or unit of atoms in a crystal is replaced by a point in space, then the resultant points in space are called space lattice. Each point in a space lattice is called a lattice point and each atom or unit of atoms is called basis or pattern. A space lattice represents the geometrical pattern of crystal in which the surroundings of each lattice point is the same. If the surroundings of each lattice point is same or if the atom or all the atoms at lattice points are identical, then such a lattice is called Bravais lattice. On the other hand, if the atom or the atoms at lattice points are not same, then it is said to be a non-Bravais lattice. Figure 7 shows a two-dimensional lattice.

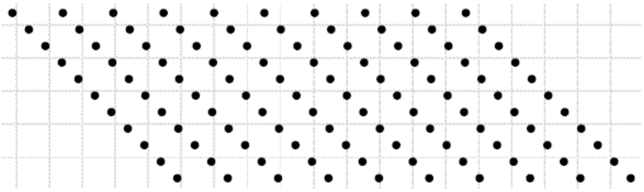


Fig. (7): A two- dimensional lattice.

In the same manner, it is very convenient to imagine periodic arrangement of points in space in 3-dimensions about which these atoms are located. “***A space lattice or a crystal lattice is defined as a three dimensional infinite array of points in space in which every point has surroundings identical to that of every other point in the array”.***

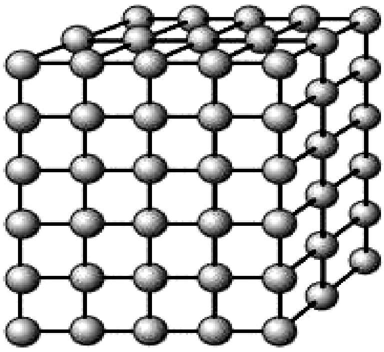


Fig. (8): A tree- dimensional lattice.

-Basis and Crystal Structure

The atomic arrangement in a crystal is called crystal structure. The crystal structure is formed by associating every lattice point with an atom or an assembly of atoms or molecules or ions, which are identical in composition, arrangement and orientation, called the basis. i.e. an atom, or a group of atoms or molecules identical in composition is called the basis or the pattern. The basis provides the number of atoms per lattice point, their types, mutual orientations and distances of separation between the atoms. If the basis is substituted for the lattice points, then the resulting structure is called crystal structure as shown in Fig. 9 below. Thus,

crystal structure = Lattice + basis.

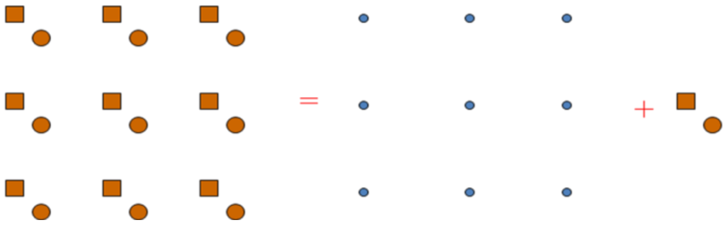


Fig. (9): crystal structure

A lattice is an imaginary assumption while the crystal structure is a real concept.

-Unit Cell

Unit cells for most of the crystals are parallelepipeds or cubes having three sets of parallel faces. A unit cell is the basic structural unit or building block of the crystal. A unit cell is defined as the smallest parallelepiped volume in the crystal, which on repetition along the crystallographic axes gives the actual crystal structure or the smallest geometric figure, which on repetition in three dimensional space, gives the actual crystal structure is called a unit cell.

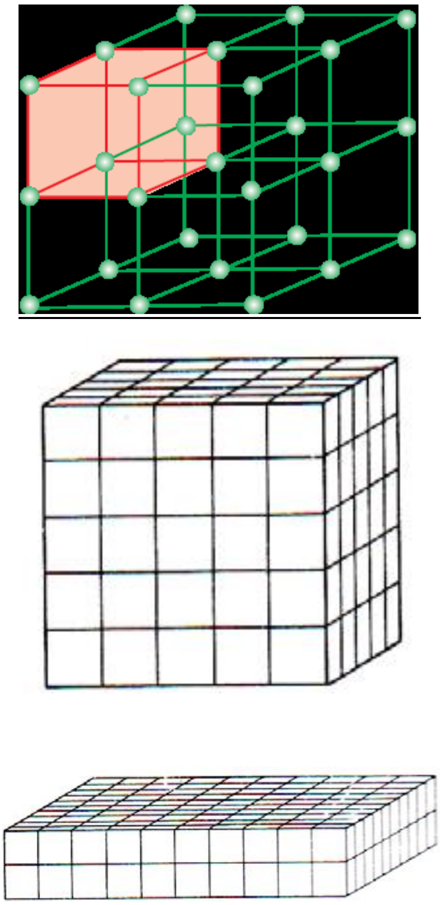


Fig. (10): Unit cell

The choice of a unit cell is not unique but it can be constructed in a number of ways; Fig. 11 shows different ways of representing unit cells in a two-dimensional lattice. A unit cell can be represented as square, rectangle, diamond, hexagonal and oblique shapes.

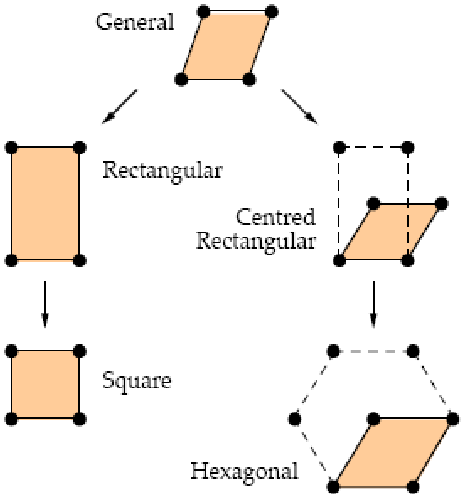


Fig. (11): Unit cells in a two-dimensional lattice.

-Lattice parameters

The lattice constant [or lattice parameter] refers to the constant distance between unit cells in a crystal lattice. Lattices in three dimensions generally have three lattice constants, referred to as *a*, *b*, and *c*. However, in the special case of cubic crystal structures, all of the constants are equal and we only refer to *a*. Similarly, in hexagonal crystal structures, the *a* and *b* constants are equal, and we only refer to the *a* and *c* constants. A group of lattice constants could be referred to as lattice parameters. However, the full set of lattice parameters consist of the three lattice constants and the three angles between them.

To define the unit cell parameters or lattice parameters, first we define crystallographic axes.

These axes are obtained by the intersection of the three non-coplanar faces of the unit cell. The angles between these faces or crystallographic axes are known as interfacial or interaxial angles. The angles between the axes Y and Z is α, between Z and X is β and between X and Y is γ. The translational vectors or primitives a, b, c of a unit cell along X, Y, Z axes and interaxial angles α, β, γ are called cell parameters. These cell parameters are shown in Figure below. The cell parameters determine the actual size and shape of the unit cell.

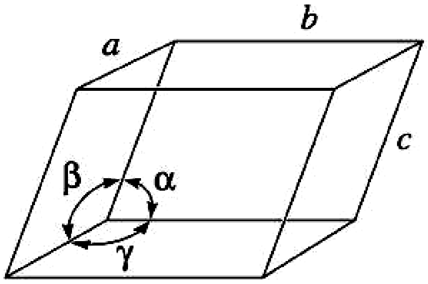


Fig. (12): Unit cell parameters

-Primitive and non-primitive unit cells: The unit cell formed by primitives is called a simple or a primitive unit cell. A primitive unit cell contains only one lattice point. If a unit cell contains more than one lattice point, then it is called a non-primitive unit cell or a multiple unit cell. Most of the unit cells of various crystal lattices contain two or more lattice points and hence it is not necessary that unit cell should be a primitive unit cell. For example, BCC and FCC are non-primitive unit cells.

-Bravais Lattice: If the surroundings of each lattice point is same or if the atom or all the atoms at lattice points are identical, then such a lattice is called Bravais lattice. Based on the number of lattice points present per unit cell and stacking sequence of base atoms in a crystal structure, the Bravais lattices are classified into Simple or Primitive (P), Body Centered (I), Face Centered (F) and Base Centered (C) lattices. In simple or primitive lattice, 8 lattice points or 8 atoms are present at the 8 corners of the unit cell, each contributing 1/8th to the unit cell and hence there will be 8 x

1/8 = 1 lattice point per unit cell. In body-centered lattice, in addition to the 8 atoms at 8 corners each contributing 1/8th to the unit cell, there will be one complete atom at the center of the unit cell. Therefore number of atoms or lattice points in a body centered unit cell becomes 8 x 1/8 + 1 x 1 = 2. In case of face-centered lattice, in addition to the 8 atoms at 8 corners each contributing 1/8th to the unit cell, six atoms will be present at the center of six faces of the cell each contributing 1/2nd to the unit cell. Therefore number of atoms or lattice points in a face centered unit cell becomes 8 x 1/8 + 6 x 1/2 = 4. Similarly, in case of base-centered lattice, in addition to the 8 atoms at 8 corners each contributing 1/8th to the unit cell, two atoms will be present at the center of upper and lower faces of the unit cell each contributing 1/2nd to the unit cell and hence the number of atoms or lattice points in a base centered unit cell becomes 8 x 1/8 + 2 x 1/2 = 2.

-Hexagonal Closed Packed structure (HCP) :

The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this mid-plane have as nearest neighbors atoms in both of the adjacent two planes. The equivalent of six atoms is contained in each unit cell; one-sixth of each of the 12 top and bottom face corner atoms, one-half of each of the 2 center face atoms, and all 3 mid-plane interior atoms.

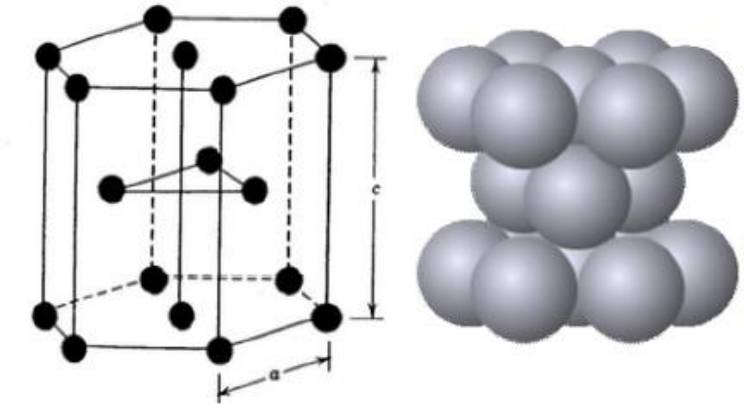


Fig. (13): Hexagonal Closed Packed structure (HCP).

- Crystal Systems and Bravais Lattices:

For representing the type of distribution of lattice points in space, seven different co-ordinate systems are required. These co-ordinate systems are called crystal systems. The crystal systems are named on the basis of geometrical shape and symmetry. The seven crystal systems are: (1) Cubic (2) Tetragonal (3) Orthorhombic (4) Monoclinic (5) Triclinic (6) Trigonal (or Rhombohedral) and (7) Hexagonal. Space lattices are classified according to their symmetry. In 1948, Bravais showed that 14 lattices are sufficient to describe all crystals. These 14 lattices are known as Bravais lattices and are classified into 7 crystal systems based on cell parameters. The Bravais lattices are categorized as primitive lattice (P); body-centered lattice (I); face-centered lattice (F) and base-centered lattice (C). These seven crystal systems and Bravais lattices are described below.

1. Cubic crystal system: In this crystal system, all the unit cell edge lengths are equal and are at right angles to one another i.e., $a = b = c$ and $\alpha = \beta = \gamma = 90°$. In cubic system, there are three Bravais lattices; they are simple (primitive); body-centered and face-centered.
Examples for cubic system are Au, Cu, Ag, NaCl, diamond, etc.

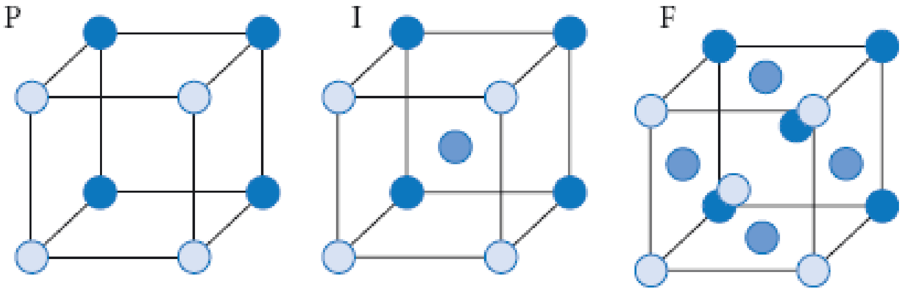


Fig. (14): Bravais lattices in cubic system

2. Tetragonal crystal system: In this crystal system, two lengths of the unit cell edges are equal whereas the third length is different. The three edges are perpendicular to one another i.e., $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$. In tetragonal system, there are two Bravais lattices; they are simple and body-centered. These are shown in Figure below. Examples for tetragonal crystal systems are TiO2, SnO2, etc.

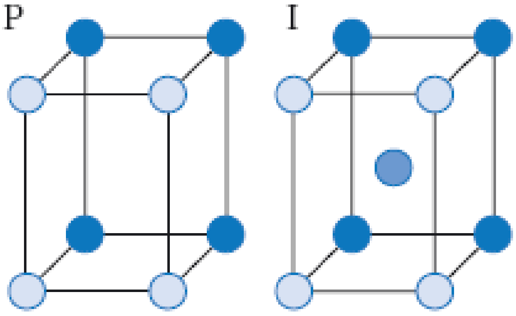


Fig. (15): Bravais lattices in Tetragonal system

3. Orthorhombic crystal system: In this crystal system, unit cell edge lengths are different and they are perpendicular to one another i.e., $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$. There are four Bravais lattices in this system. They are simple, face centered, body centered and base centered. These are shown in Figure below. Examples for orthorhombic crystal system are BaSO4, K2SO4, SnSO4, etc.

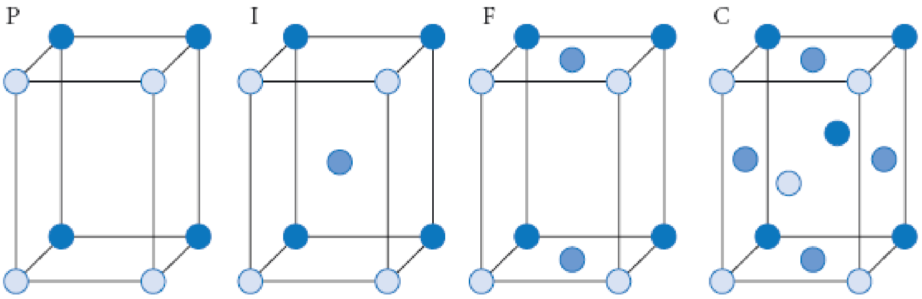


Fig. (16): Bravais lattices in Orthorhombic system

4. Monoclinic crystal system: In this crystal system, the unit cell edge lengths are different. Two unit cell edges are not perpendicular, but they are perpendicular to the third edge i.e., $a \neq b \neq c$; $\alpha = \gamma = 90° \neq \beta$. This crystal system has two Bravais lattices; they are simple and base centered. These are shown in Figure below. Examples for Monoclinic crystal system are CaSO4.2H2O (gypsum), Na3AlF6 (cryolite), etc.

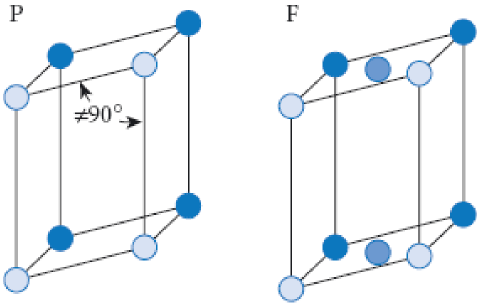


Fig. (17): Bravais lattices in Monoclinic system

5. Triclinic crystal system: In this crystal system, the unit cell edge lengths are different and are not perpendicular i.e., $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$ and all the angles are different. This crystal exists in primitive cell only. This is shown in Figure below. Examples for triclinic crystal system are K2Cr2O7, CuSO4. 5H2O, etc.

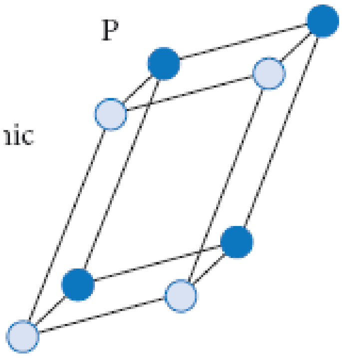


Fig. (18): Bravais lattices in Triclinic system

6. Trigonal or Rhombohedral crystal system: In this crystal system, all the lengths of unit cell edges are equal. The angles between the axes are equal but other than 90° i.e., $a = b = c$ and $\alpha = \beta =$

$\gamma \neq 90°$. The Bravais lattice is simple only as shown in Figure below. Examples for Rhombohedral crystal system are As, Bi, Sb, etc.

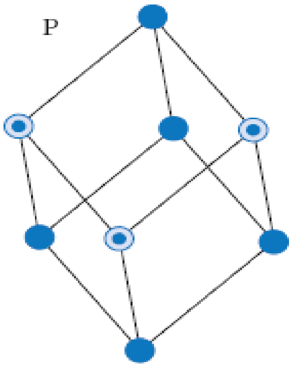


Fig. (19): Bravais lattices in Trigonal system

7. Hexagonal crystal system: In this crystal system, two sides of the unit cell edge lengths are equal and the angle between these edges is 120°. These two edges are perpendicular to the third edge, and not equal in length i.e., $a = b \neq c$ and $\alpha = \beta = 90°$; $\gamma = 120°$. The Bravais lattice is primitive only. This is shown in Fig. 1.12. The atoms in this crystal system are arranged in the form of a hexagonal close pack.

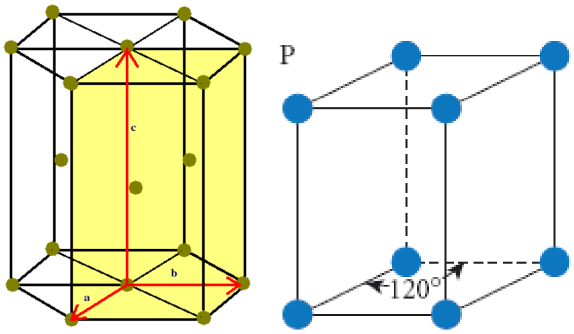


Fig. (20): Bravais lattices in Hexagonal system

By assigning specific values for axial lengths and interaxial angles, unit cells of different types can be constructed. These crystal systems are listed in the following table:

Table (1): Classification of Space Lattices by Crystal System

Crystal system	**Axial lengths and angles**	**Space lattice**
Cubic	$a = b = c,$ $\alpha = \beta = \gamma = 90$	Simple Body-centered Face-centered
Tetragonal	$a = b \neq c,$ $\alpha = \beta = \gamma = 90$	Simple Body-centered
Orthorhombic	$a \neq b \neq c,$ $\alpha = \beta = \gamma = 90$	Simple Body-centered Base-centered Face-centered
Rhombohedral	$a_1 = a_2 = a_3 \neq c,$ $\alpha = \beta = 90, \ \gamma = 120^\circ$	Simple
Hexagonal	$a_1 = a_2 = a_3 \neq c,$ $\alpha = \beta = 90 , \ \gamma = 120^\circ$	Simple
Monoclinic	$a \neq b \neq c,$ $\alpha = \gamma = 90 \neq \beta$	Simple Base-centered
Triclinic	$a \neq b \neq c,$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple

Crystal Symmetry

Crystals possess a regular, repetitive internal structure. The concept of symmetry describes the repetition of structural features. Crystals therefore possess symmetry, and much of the discipline of crystallography is concerned with describing and cataloging different types of symmetry.

Two general types of symmetry exist. These consist of translational symmetry and point symmetry. Translational symmetry (internal operation) describes the periodic repetition of a structural feature across a length or through an area or volume. Point symmetry (external operation), on the other hand, describes the periodic repetition of a structural feature around a point. Reflection, rotation, and inversion are all point symmetries.

TRANSLATION OPERATIONS

Periodic repetitions along vectors or translations of ions can be achieved in 1-D, 2-D and 3-D producing row-lattices, plane-lattices and space-lattices, respectively. These are internal symmetry operations and do not occur as symmetry element.

Row-Lattices: are produced by translation along single vector. Here ions are repeated with constant distances along a line. (FIG. 4.14)

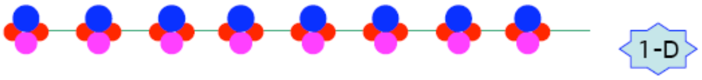


Fig. (21): 1-D Row-Lattices

Plane-Lattices: are produced by translations along two vectors. Here ions are repeated with constant distances and angles that produce 5 unique plane-lattices. (FIG. 4.15)

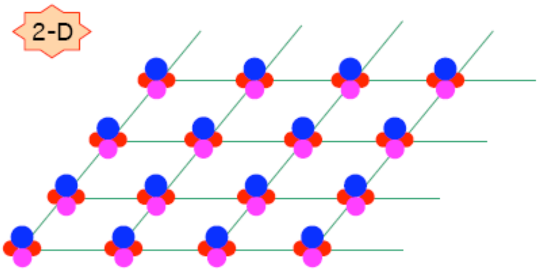


Fig. (22): 2-D plane-Lattices

Space-Lattices: are produced by translations along three vectors. Here ions are repeated again with constant distances and angles in 3-D that produce 14 unique space-lattices, which are also known as Bravais Lattices (FIG. 4.16). They are compatible with 6 symmetry systems and 32 symmetry classes.

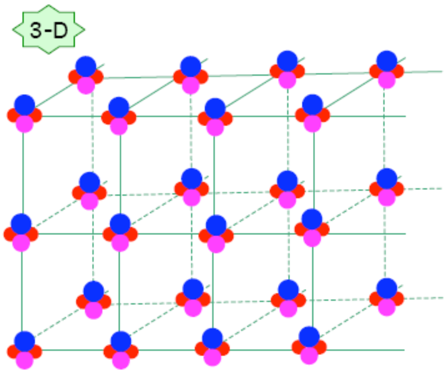


Fig. (23): 3-D space-Lattices

External Symmetry Operations

A Symmetry operation is an operation that can be performed either physically or imaginatively and results in no change in the appearance of an object. Again it is emphasized that in crystals, the symmetry is internal, that is it is an ordered geometrical arrangement of atoms and molecules on the crystal lattice. But, since the internal symmetry is reflected in the external form of perfect crystals, we are going to concentrate on external symmetry, because this is what we can observe.

There are 3 types of symmetry operations: rotation, reflection, and inversion. We will look at each of these in turn.

Rotational Symmetry

As illustrated above, if an object can be rotated about an axis and repeats itself every 90^o of rotation then it is said to have an axis of 4-fold rotational symmetry. The axis along which the rotation is performed is an element of symmetry referred to as a rotation axis. The following types of rotational symmetry axes are possible in crystals.

1-Fold Rotation Axis - An object that requires rotation of a full 360^o in order to restore it to its original appearance has no rotational symmetry. Since it repeats itself 1 time every 360^o it is said to have a 1-fold axis of rotational symmetry.

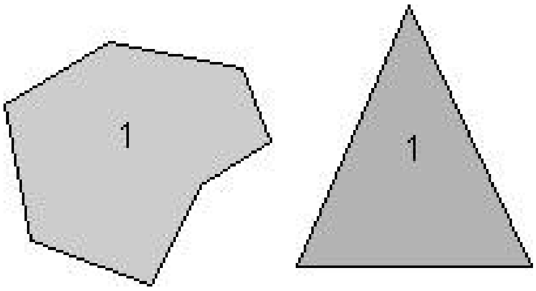


Fig. (24): 1-Fold Rotation Axis

2-fold Rotation Axis - If an object appears identical after a rotation of 180^o, that is twice in a 360^o rotation, then it is said to have a 2-fold rotation axis (360/180 = 2). Note that in these examples the axes we are referring to are imaginary lines that extend toward you perpendicular to the page or blackboard. A filled oval shape represents the point where the 2-fold rotation axis intersects the page.

This symbolism will be used for a 2-fold rotation axis throughout the lectures and in your text.

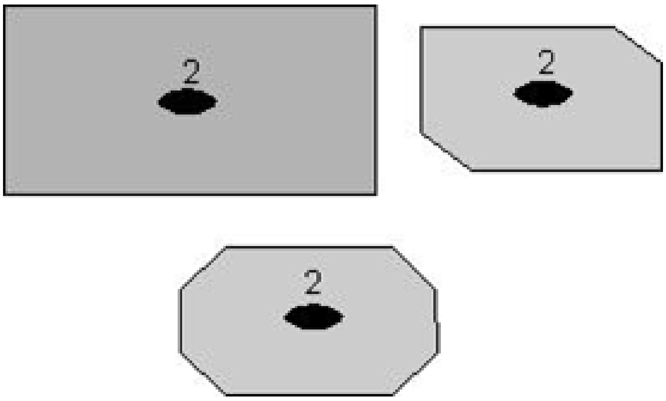


Fig. (25): 2-Fold Rotation Axis

3-Fold Rotation Axis- Objects that repeat themselves upon rotation of 120^{o} are said to have a 3-fold axis of rotational symmetry (360/120 =3), and they will repeat 3 times in a 360o rotation. A filled triangle is used to symbolize the location of 3-fold rotation axis.

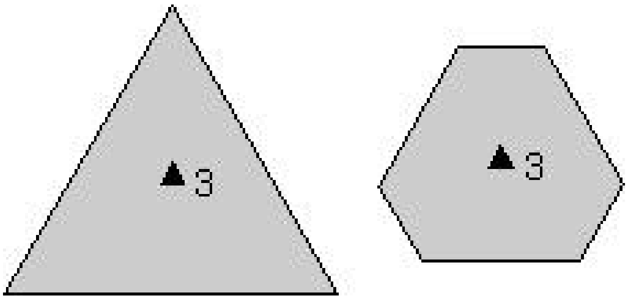


Fig. (26): 3-Fold Rotation Axis

4-Fold Rotation Axis - If an object repeats itself after 90^{o} of rotation, it will repeat 4 times in a 360^{o}rotation, as illustrated previously. A filled square is used to symbolize the location of 4-fold axis of rotational symmetry.

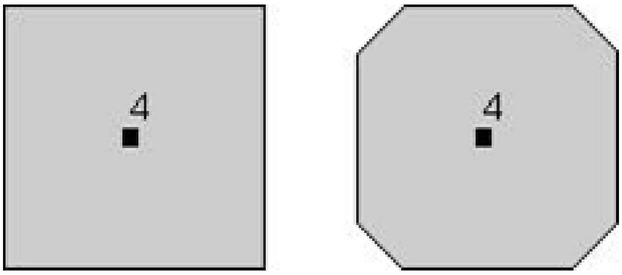


Fig. (27): 4-Fold Rotation Axis

6-Fold Rotation Axis - If rotation of 60^{o} about an axis causes the object to repeat itself, then it has 6-fold axis of rotational symmetry (360/60=6). A filled hexagon is used as the symbol for a 6-fold rotation axis.

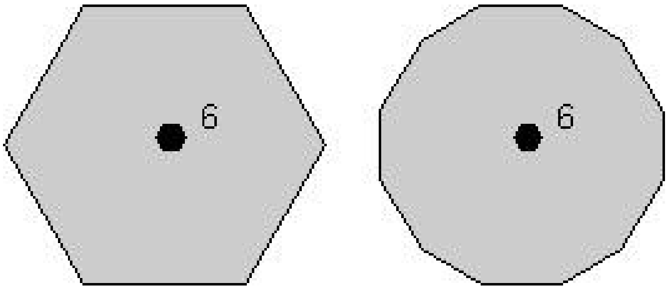


Fig. (28): 6-Fold Rotation Axis

Although objects themselves may appear to have 5-fold, 7-fold, 8-fold or higher-fold rotation axes, these are not possible in crystals. The reason is that the external shape of a crystal is based on a geometric arrangement of atoms. Note that if we try to combine objects with 5-foldand 8-fold apparent symmetry, that we cannot combine them in such a way that they completely fill space, as illustrated below.

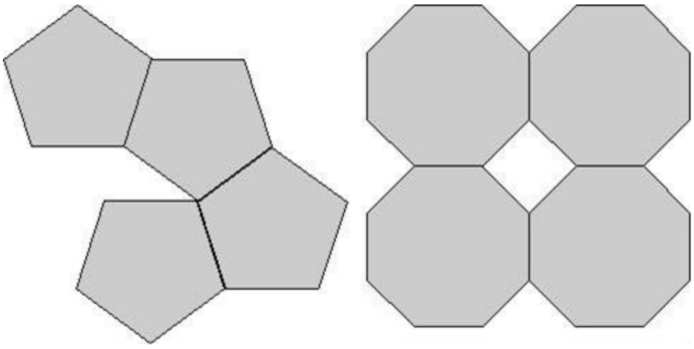


Fig. (29): 5-fold, 7-fold, 8-fold or higher-fold rotation axes are not possible

Mirror Symmetry

A mirror symmetry operation is an imaginary operation that can be performed to reproduce an object. The operation is done by imagining that you cut the object in half, and then place a mirror next to one of the halves of the object along the cut. If the reflection in the mirror reproduces the other half of the object, then the object is said to have mirror symmetry. The plane of the mirror is an element of symmetry referred to as a mirror plane, and is symbolized with the letter m. As an example, the human body is an object that approximates mirror symmetry, with the mirror plane cutting through the center of the head, the center of nose and down to the groin.

The rectangles showed below have two planes of mirror symmetry.

The rectangle on the left has a mirror plane that runs vertically on the page and is perpendicular to the page. The rectangle on the right has a mirror plane that runs horizontally and is perpendicular to the page.

The dashed parts of the rectangles below show the part the rectangles that would be seen as a reflection in the mirror.

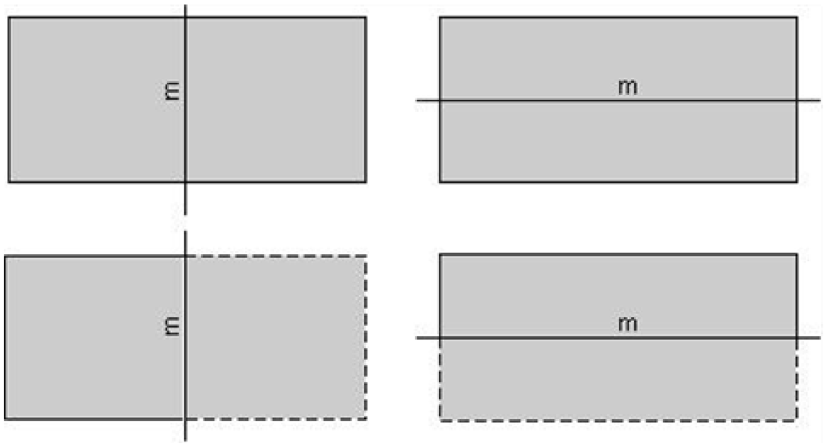


Fig. (30): Mirror Symmetry

The rectangles showed above have two planes of mirror symmetry. Three dimensional and more complex objects could have more. For example, the hexagon shown above, not only has a 6-fold rotation axis, but has 6 mirror planes.

Note that a rectangle does not have mirror symmetry along the diagonal lines. If we cut the rectangle along a diagonal such as that labeled "m ???", as shown in the upper diagram, reflected the lower half in the mirror, then we would see what is shown by the dashed lines in lower diagram. Since this does not reproduce the original rectangle, the line "m???" does not represent a mirror plane.

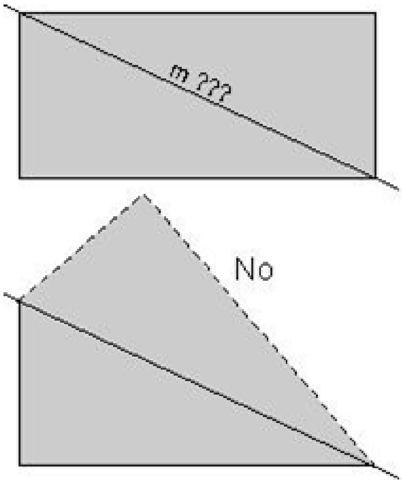


Fig. (31): No Mirror Symmetry

Center of Symmetry

Another operation that can be performed is inversion through a point. In this operation lines are drawn from all points on the object through a point in the center of the object, called asymmetry center (symbolized with the letter "i").The lines each have lengths that are equidistant from the original points. When the ends of the lines are connected, the original object is reproduced inverted from its original appearance. In the diagram shown here, only a few such lines are drawn for the small triangular face. The right hand diagram shows the object without the imaginary lines that reproduced the object.

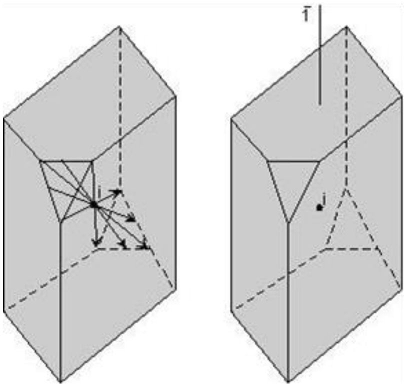


Fig. (32): Center of Symmetry

If an object has only a center of symmetry, we say that it has a 1 fold rotoinversion axis. Such an axis has the symbol, as shown in the right hand diagram above. Note that crystals that have a center of symmetry will exhibit the property that if you place it on a table there will be a face on the top of the crystal that will be parallel to the surface of the table and identical to the face resting on the table.

Rotoinversion

Combinations of rotation with a center of symmetry perform the symmetry operation of rotoinversion. Objects that have rotoinversion symmetry have an element of symmetry called a rotoinversion axis. A 1-fold rotoinversion axis is the same as a center of symmetry, as discussed above. Other possible rotoinversion are as follows:

2-fold Rotoinversion - The operation of 2-fold rotoinversion involves first rotating the object by 180^{o} then inverting it through an inversion center. This operation is equivalent to having a mirror plane perpendicular to the 2-fold rotoinversion axis. A 2-fold rotoinversion axis is symbolized as a 2 with a bar over the top, and would be pronounced as "bar 2". But, since this the equivalent of a mirror plane, m, the bar 2 is rarely used.

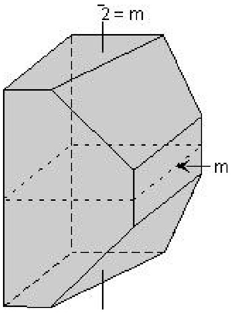


Fig. (33): 2-fold Rotoinversion

3-fold Rotoinversion - This involves rotating the object by 120^o(360/3 = 120), and inverting through a center. A cube is good example of an object that possesses 3-fold rotoinversion axes. A3-fold rotoinversion axis is denoted as (pronounced "bar 3").

Note that there are actually four axes in a cube, one running through each of the corners of the cube. If one holds one of the axes vertical, then note that there are 3 faces on top, and 3 identical faces upside down on the bottom that are offset from the top faces by 120^o.

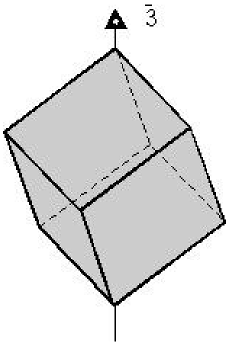


Fig. (34): 3-fold Rotoinversion

4-fold Rotoinversion - This involves rotation of the object by 90^o then inverting through a center. A 4-fold rotoinversion axis is symbolized as. Note that an object possessing a 4- fold rotoinversion axis will have two faces on top and two identical faces upside down on the bottom, if the axis is held in the vertical position.

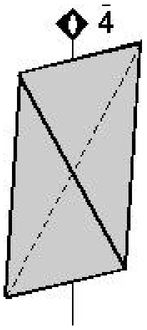


Fig. (35): 4-fold Rotoinversion

6-fold Rotoinversion - A 6-fold rotoinversion axis ( ) involves rotating the object by 60o and inverting through a center. Note that this operation is identical to having the combination of a 3-fold rotation axis perpendicular to a mirror plane.

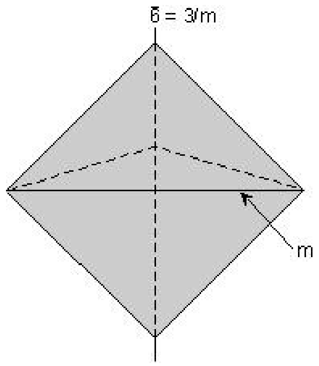


Fig. (36): 6-fold Rotoinversion

Combinations of Symmetry Operations

As should be evident by now, in three dimensional objects, such as crystals, symmetry elements may be present in several different combinations. In fact, in crystals there are 32 possible combinations of symmetry elements. These 32 combinations define the 32 Crystal Classes. Every crystal must belong to one of these 32 crystal classes. In the next lecture we will start to go over each of these crystal classes in detail, but the best way to be able to identify each crystal class is not by listening to me lecture, not necessarily by reading about each class, but actually looking at models of perfect crystals in the lab. In fact, it is my opinion that it is next to impossible to identify symmetry elements and crystal classes without spending a lot of time examining and studying the 3-dimensional models in lab.

Here, an example of how the various symmetry elements are combined in a somewhat completed crystal. One point that I want to emphasize in this discussion is that if 2 kinds of symmetry elements are present in the same crystal, then they will operate on each other to produce other symmetrical symmetry elements. This should become clear as we go over the example below.

In this example we will start out with the crystal shown here. Note that this crystal has rectangular-shaped sides with a square- shaped top and bottom. The square-shaped top indicates that there must be a 4-fold rotation axis perpendicular to the square shaped face. This is shown in the diagram.

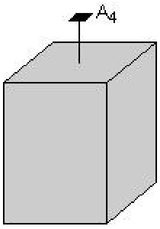


Fig. (37): A 4-fold rotation axis perpendicular to the square shaped face

Also note that the rectangular shaped face on the left side of the crystal must have a 2-fold rotation axis that intersects it. Note that the two fold axis runs through the crystal and exits on the left-hand side (not seen in this view), so that both the left and right -hand sides of the crystal are perpendicular to a 2-fold rotation axis.

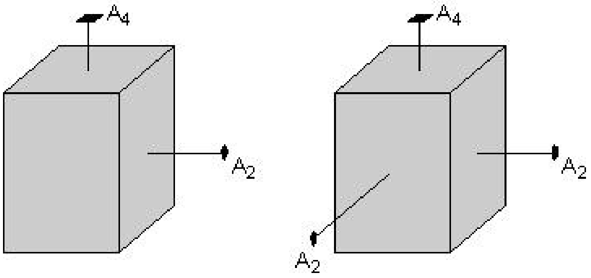


Fig. (38): The left and right -hand sides of the crystal are perpendicular to a 2-fold rotation axis.

Since the top face of the crystal has a 4-fold rotation axis, operation of this 4-fold rotation must reproduce the face with the perpendicular 2-fold axis on a 90o rotation. Thus, the front and back faces of the crystal will also have perpendicular 2-fold rotation axes, since these are required by the 4-fold axis.

The square-shaped top of the crystal also suggests that there must be a 2-fold axis that cuts diagonally through the crystal.

This 2-fold axis is shown here in the left-hand diagram. But, again operation of the 4-fold axis requires that the other diagonals also have 2-fold axis, as shown in the right-hand diagram.

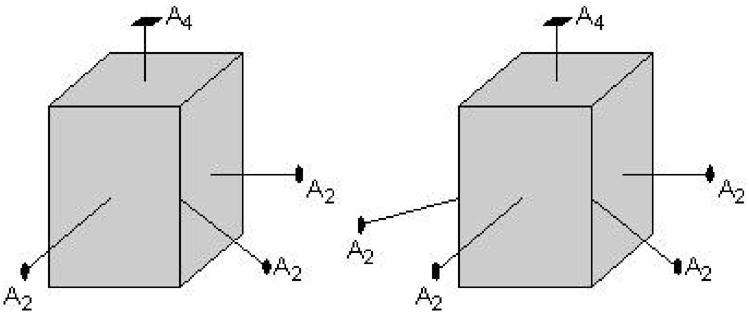


Fig. (39): There must be a two 2-fold axis that cuts diagonally through the crystal.

Furthermore, the square-shaped top and rectangular-shaped front of the crystal suggest that a plane of symmetry is present as shown by the left-hand diagram here. But, again, operation of the 4-fold axis requires that a mirror plane is also present that cuts through the side faces, as shown by the diagram on the right.

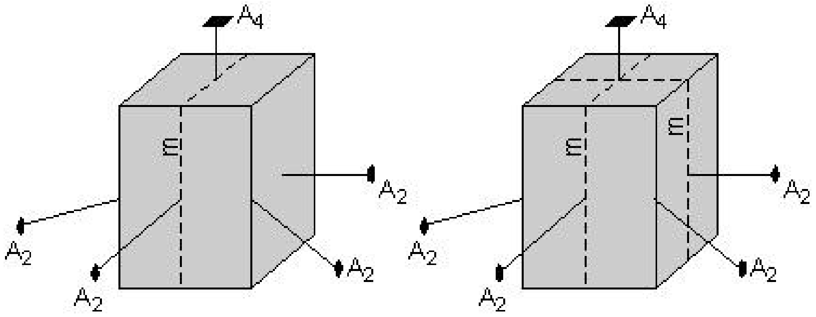


Fig. (40): Two mirror planes are also present that cut through the side faces

The square top further suggests that there must be a mirror plane cutting the diagonal through the crystal. This mirror plane will be reflected by the other mirror planes cutting the sides of the crystal, or will be reproduced by the 4-fold rotation axis, and thus the crystal will have another mirror plane cutting through the other diagonal, as shown by the diagram on the right.

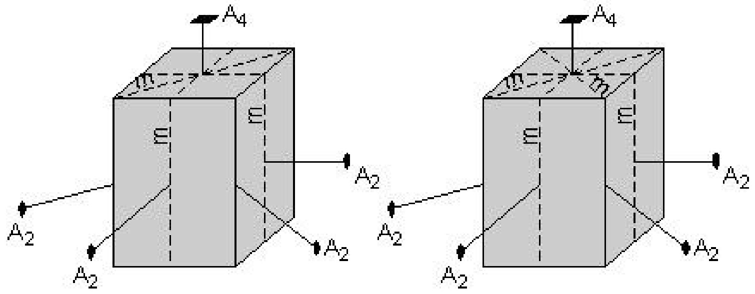


Fig. (41): Two other mirror planes are also present that cut through the diagonals of the crystal

Finally, there is another mirror plane that cuts through the center of the crystal parallel to the top and bottom faces.

Thus, this crystal has the following symmetry elements:

1 - 4-fold rotation axis (A4)

4 - 2-fold rotation axes (A2), 2 cutting the faces & 2 cutting the edges.

5- mirror planes (m), 2 cutting across the faces, 2 cutting through the edges, and one cutting horizontally through the center.

Note also that there is a center of symmetry (i).

The symmetry content of this crystal is thus: i, 1A4, 4A2, 5m

If you look at the table (Table 6.3 on page 120 of Klein, you should see that this belongs to crystal class 4/m2/m2/m. This class is the ditetragonal dipyramidal class. We will discuss this notation and the various crystals classes in the next lecture.

We've now seen how crystallographic axes can be defined for the various crystal systems. Two important points to remember are that

1. The lengths of the crystallographic axes are controlled by the dimensions of the unit cell upon which the crystal is based.

2. The angles between the crystallographic axes are controlled by the shape of the unit cell.

We also noted last time that the relative lengths of the crystallographic axes control the angular relationships between crystal faces. This is true because crystal faces can only develop along lattice points. The relative lengths of the crystallographic axes are called axial ratios, our first topic of discussion.

The 32 Crystal Classes

The reflection, rotation, inversion, and rotoinversion symmetry operations may be combined in thirty-two different ways. Thirty-two different crystal classes are therefore defined so that each crystal class corresponds to a unique set of symmetry operations. Each of the crystal classes is named according to the variant of a crystal form which it displays. For example, the isometric hexoctahedral class belongs to the isometric crystal system and demonstrates the hexoctahedral crystal form. The rhombic pyramidal, tetragonal pyramidal, trigonal pyramidal and hexagonal pyramidal classes each display a variant of the crystal form which is called a pyramid. Each crystal class is a member of one of the seven different crystal systems according to which characteristic symmetry operation it possesses. For example, all crystals of the isometric system possess four 3-fold axes of symmetry, while minerals of the tetragonal system possess a single 4-fold symmetry axis and crystals of the triclinic class show no symmetry at all. The rhombic pyramidal crystal class is thus a member of the orthorhombic crystal system, the tetragonal pyramidal class is a member of the tetragonal crystal system, and the trigonal and hexagonal pyramidal classes are members of the rhombohedral (trigonal) and hexagonal divisions of the hexagonal crystal system respectively.

The following table lists the seven crystal systems. Included are the Isometric, Hexagonal, Trigonal, Tetragonal, Orthorhombic, Monoclinic, and Triclinic systems. Under each crystal system the table lists by name the crystal classes which occur within that system. For example, the crystal classes which occur within the Trigonal crystal system are the Trigonal monohedral and Trigonal parallelohedral crystal classes. Adjacent to the listing of each crystal class is the symmetry content of the class. When listing the symmetry of each crystal class an axis of rotational symmetry is represented by the capital letter A. Whether this axis is a 2-fold, 3-fold, or 4-fold axis is indicated by a subscript following the letter A. The number of such axes present is indicated by a numeral preceding the capital A. 1A2, 2A3, and 3A4 thus represent one 2-fold axis of rotation, two 3-fold axes, and three 4-fold axes respectively. A center of inversion is noted by the lowercase letter 'i' while a mirror plane is denoted by 'm'. The numeral preceding the m indicates how many mirror planes are present. Axes of rotary inversion are usually replaced by the equivalent rotations and reflections. For example, a 2-fold rotoinversion axis is equivalent to reflection through a mirror plane perpendicular to the rotoinversion axis. A crystal which possesses a 3-fold rotoinversion axis is equivalent to one which possesses both 3-fold rotational symmetry and inversion symmetry. A 6-fold rotoinversion is equivalent to 3-fold rotation and reflection across a mirror plane at right angles to the rotation axis. The only rotoinversion operation which cannot be thus replaced is 4-fold rotoinversion, which is indicated by R4. The class which possesses the highest possible symmetry within each crystal system is termed the holomorphic class of that system. The holomorphic class of each crystal system is indicated in the table by bold type. For example, the triclinic parallelohedron is the holomorphic class of the triclinic crystal system while the isometric hexoctahedron is the holomorphic class of the isomorphic or cubic crystal system. The characteristic symmetry element of each crystal system is listed in bold type. It is thus apparent that the characteristic symmetry element of the isometric crystal system is the possession of four 3-fold axes of rotational symmetry, while the characteristic symmetry element of the rhombohedral system is the possession of a single 3-fold axis of rotational symmetry.

Table (2): Crystal systems, classes and their contained symmetry.

Crystal System	Crystal Class / Crystal Form	Symmetry of Class
Isometric System	hexoctahedron	i, 3A4, 4A3, 6A2, 9m
	gyroid	3A4, 4A3, 6A2
	hextetrahedron	3A2, 4A3, 6m
	diploid	i, 3A2, 4A3, 3m
	tetartoid	3A2, 4A3
Hexagonal System	dihexagonal dipyramid	i, 1A6, 6A2, 7m
	hexagonal trapezohedron	1A6, 6A2
	dihexagonal pyramid	1A6, 6m
	ditrigonal dipyramid	1R6, 3A2, 3m

	hexagonal dipyramid	i, 1A6, 1m
	hexagonal pyramid	1A6
	trigonal dipyramid	1R6
Trigonal System	hexagonal scalenohedron	i, 1A3, 3A2, 3m
	trigonal trapezohedron	1A3, 3A2
	ditrigonal pyramid	1A3, 3m
	rhombohedron	i, 1A3
	trigonal pyramid	1A3
Tetragonal System	ditetragonal dipyramid	i, 1A4, 4A2, 5m
	tetragonal trapzohedron	1A4, 4A2
	ditetragonal pyramid	1A4, 4m
	tetragonal scalenohedron	1R4, 2A2, 2m
	tetragonal dipyramid	i, 1A4, 1m
	tetragonal pyramid	1A4
	tetragonal disphenoid	1R4
Orthorhombic System	rhombic dipyramid	i, 3A2, 3m
	rhombic disphenoid	3A2
	rhombic pyramid	1A2, 2m
Monoclinic System	prism	i, 1A2, 1m
	sphenoid	1A2
	dome	1m
Triclinic System	parallellohedron	i
	monohedron	no symmetry

Axial Ratios

Axial ratios are defined as the relative lengths of the crystallographic axes. They are normally taken as relative to the length of the b crystallographic axis. Thus, an axial ratio is defined as follows:

$$\text{Axial Ratio} = a/b\text{: } b/b\text{: } c/b$$

where a is the actual length of the a crystallographic axis, b, is the actual length of the b crystallographic axis, and c is the actual length of the c crystallographic axis.

For Triclinic, Monoclinic, and Orthorhombic crystals, where the lengths of the three axes are different, this reduces to: a/b : 1 : c/b (this is usually shortened to a : 1 : c)

For Tetragonal crystals where the length of the a and b axes are equal, this reduces to: 1 : 1 : c/b (this is usually shorted to 1 : c)

For Isometric crystals where the length of the a, b, and c axes are equal this becomes: 1 : 1 : 1 (this is usually shorted to 1)

For Hexagonal crystals where there are three equal length axes (a1, a2, and a3) perpendicular to the c axis this becomes: 1: 1: 1: c/a (usually shortened to 1: c)

Modern crystallographers can use x-rays to determine the size of the unit cell, and thus can determine the absolute value of the crystallographic axes. For example, the mineral quartz is hexagonal, with the following unit cell dimensions as determined by x-ray crystallography: a1= a2 = a3 = 4.913Å, c = 5.405Å

where Å stands for Angstroms = 10^{-10} meter.

Thus the axial ratio for quartz is

1: 1: 1: 5.405/4.913 or 1: 1 : 1 : 1.1001

which simply says that the c axis is 1.1001 times longer than the a axes.

For orthorhombic sulfur the unit cell dimensions as measured by x-rays are:

a = 10.47Å, b = 12.87Å, c = 24.39Å

Thus, the axial ratio for orthorhombic sulfur is:

10.47/12.87: 12.87/12.87: 24.39/12.87 or 0.813: 1: 1.903

Because crystal faces develop along lattice points, the angular relationship between faces must depend on the relative lengths of the axes. Long before x-rays were invented and absolute unit cell dimensions could be obtained, crystallographers were able to determine the axial ratios of minerals by determining the angles between crystal faces. So, for example, in 1896 the axial ratios of orthorhombic sulfur were determined to be nearly exactly the same as those reported above from x-ray measurements.

In a later lecture we will see how we can determine axial ratios from the angular relationships between faces. First, however we must determine how we can name or index faces of crystals and define directions within crystals.

Intercepts (Weiss Parameters)

Crystal faces can be defined by their intercepts on the crystallographic axes. For non-hexagonal crystals, there are three cases.

1. A crystal face intersects only one of the crystallographic axes.

As an example the top crystal face shown here intersects the c axis but does not intersect the a or b axes. If we assume that the face intercepts the c axis at a distance of 1 unit length, then the intercepts, sometimes called Weiss Parameters, are: ∞**a, ∞b, 1c**

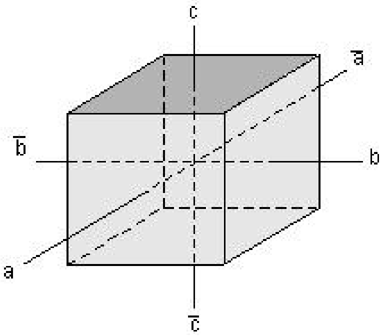


Fig. (42): A crystal face intersects only one of the crystallographic axes

2. A crystal face intersects two of the crystallographic axes.

As an example, the darker crystal face shown here intersects the a and b axes, but not the c axis.

Assuming the face intercepts the a and c axes at 1 unit cell length on each, the parameters for this face are: 1 a, 1 b, ∞c

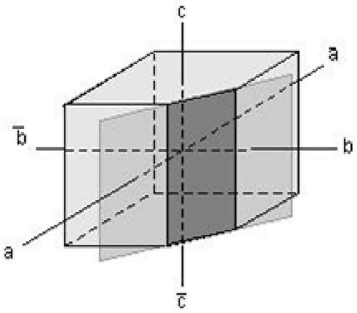


Fig. (43): A crystal face intersects two crystallographic axes

3. A crystal face that intersects all 3 axes.

In this example the darker face is assumed to intersect the a, b, and c crystallographic axes at one unit length on each. Thus, the parameters in this example would be: 1a, 1b, 1c

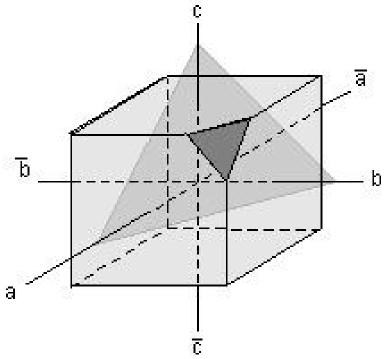


Fig. (44): A crystal face intersects the three crystallographic axes

Two very important points about intercepts of faces:

-The intercepts or parameters are relative values, and do not indicate any actual cutting lengths.

- Since they are relative, a face can be moved parallel to itself without changing its relative intercepts or parameters.

Because one does usually not know the dimensions of the unit cell, it is difficult to know what number to give the intercept of a face, unless one face is chosen arbitrarily to have intercepts with the axes and assigned the parameters - 1a, 1b, 1c. This face is called the unit face.

For example, in the orthorhombic crystal shown here, the unit face is therefore assigned the parameters 1a, 1b, 1c.

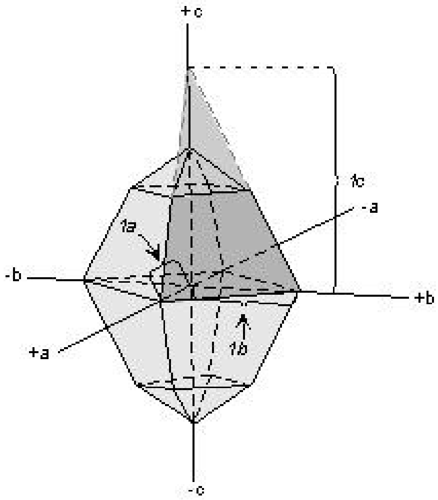


Fig. (45): parameters of the selected unit face 1a, 1b, 1c.

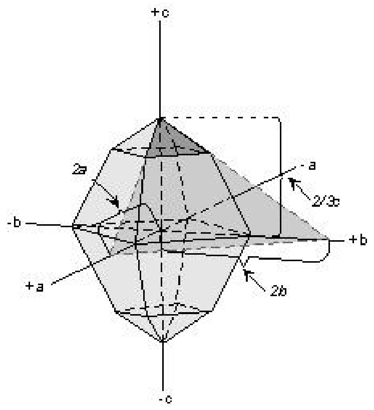


Fig. (46): Intercepts of the smaller face 2a, 2b, 2/3c.

Once the unit face is defined, the intercepts of the smaller face can be determined. These are 2a, 2b, 2/3c. Note that we can divide these parameters by the common factor 2, resulting in 1a, 1b, 1/3c. Again, this illustrates the point that moving a face parallel to itself does not change the relative do not represent the actual cutting lengths on the axes.

By specifying the intercepts or parameters of a crystal face, we now have a way to uniquely identify each face of a crystal. But, the notation is cumbersome, so crystallographers have developed another way of identifying or indexing faces. This conventional notation called the Miller Index is our next topic of discussion.

Miller Indices

The Miller Index for a crystal face is found by first determining the parameters, second inverting the parameters, and third clearing the fractions. For example, if the face has the parameters 1 a, 1 b, ∞c inverting the parameters would be 1/1, 1/1, 1/ ∞, this becomes 1, 1, 0. The Miller Index is written inside parentheses with no commas - thus (110). As further examples, let's look at the crystal shown here. All of the faces on this crystal are relatively simple. The face [labeled (111)] that cuts all three axes at 1 unit length has the parameters 1a, 1b, 1c. Inverting these, results in 1/1, 1/1, 1/1 to give the Miller Index (111).

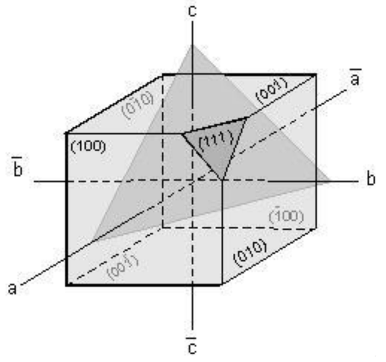


Fig. (47): The Miller Index for a crystal face.

The square face that cuts the positive a axis, has the parameters 1 a, ∞ b, ∞ c. Inverting these becomes 1/1, 1/∞**,** 1/∞ to give the Miller Index (100).

The face on the back of the crystal that cuts the negative a axis has the parameters -1a, 1/∞ b, 1/∞ c. So its Miller Index is (¯100). Note how the negative intercept is indicated by putting a minus sign above the index. This would be read "minus one, zero, zero". Thus, the other 4 faces seen on this crystal would have the Miller Indices (001), (00¯1), (010), and (0¯10).

Now let's look at some more complicated examples. The drawing below is the same orthorhombic crystal we inspect the top face that cuts all three axes had the parameters 1a, 1b,1/3c. Inverting these becomes 1/1, 1/1, 3/1 to give the Miller Index for this face as (113).

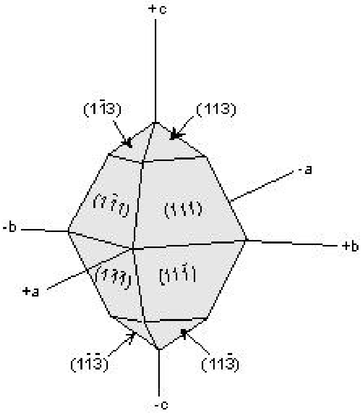


Fig. (47) cont.: A more complicated examples for the Miller Index .

Similarly, the small triangular face the cuts the positive a axis and the negative b axis, would have the Miller Index (11¯3), the similar face on the bottom of the crystal, cutting positive a, positive b, and negative c axes would have the Miller Index (11¯3).

See if you can determine the Miller Indices for the 8 faces on the back of the crystal that are not seen in this drawing. Note once again, that moving a face parallel to itself does not change the parameters nor the Miller Index for that face.

To refer to a general face that intersects all three crystallographic axes where the parameters are not known, we use the notation (hkl). For a face that intersects the b and c axes with general or unknown intercepts the notation would be (0kl), for a face intersecting the a and c axis, but parallel to b the notation would be (h0l), and similarly for a face intersecting the a and b axes, but parallel to c we would use the notation (hk0).

This Miller Index notation applies very well to crystals in the Triclinic, Monoclinic, Orthorhombic, Tetragonal, and Isometric systems, but requires some modification to be applied to the Hexagonal crystal system.

Miller Bravais Indices

Since the hexagonal system has three "a" axes perpendicular to the "c" axis, both the parameters of a face and the Miller Index notation must be modified. The modified parameters and Miller Indices must reflect the presence of an additional axis. This modified notation is referred to as Miller-Bravais Indices, with the general notation (hkil)

To see how this works, let's look at the dark shaded face in the hexagonal crystal shown here. This face intersects the positive a1axis at 1 unit length, the negative a3 axis at 1 unit length, and does not intersect the a2 or c axes. This face thus has the parameters: 1 a1, ∞a2, ˉ1 a3, ∞c, Inverting and clearing fractions gives the Miller-Bravais Index: (10ˉ10)

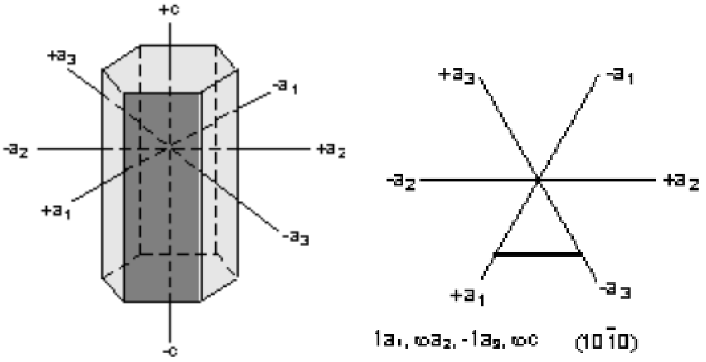


Fig. (48): Miller-Bravais Indices in the hexagonal crystal.

hexagonal system, is that whatever indices are determined for h, k, and i,

h + k + i = 0

For a similar hexagonal crystal, this time with the shaded face cutting all three axes, we would find for the shaded face in the diagram that the parameters are 1 a1, 1 a2, -1/2 a3, ∞c. Inverting these intercepts gives: 1/1, 1/1, -2/1, 1/∞ resulting in a Miller-Bravais Index of (11ˉ2 0)

Note how the "h + k + i = 0" rule applies here!

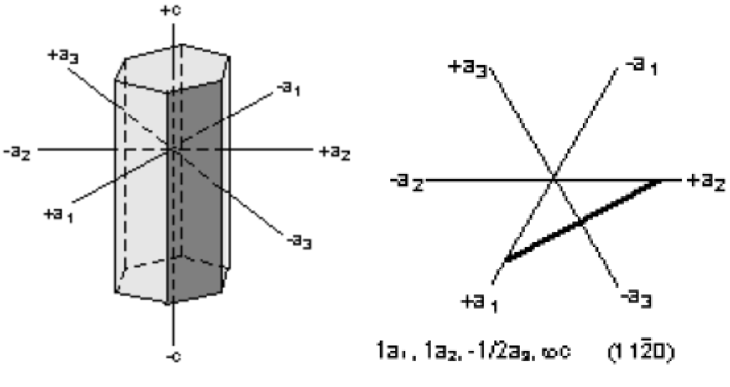


Fig. (48) cont.: Miller-Bravais Indices in the hexagonal crystal.

Crystal Forms

Now, the next step is to use the Miller Index notation to designate crystal forms. A crystal form is a set of crystal faces that are related to each other by symmetry. To designate a crystal form (which could imply many faces) we use the Miller Index, or Miller-Bravais Index notation enclosing the indices in curly braces, i.e. {hkl} or {hkil}

Such notation is called a form symbol.

As an example, look at the crystal drawing shown here. This crystal is the same orthorhombic crystal discussed above. It has two forms. The form {111} consists of the following symmetrically 8 related faces:

(111),(11¯1),(1¯1 1),(1¯1¯1),(¯111),(¯11¯1),(¯1¯1 1), and (¯1¯1¯1).

This form is called a rhombic-dipyramid.

The other form is also a rhombic-dipyramid, but consists of the triangular shaped faces similar to the face (113). The form symbol for this form is {113} and consists of the following 8 faces:

(113),(1¯1 3),(11¯3),(1¯1¯3),(¯113), (¯11¯3), (¯1¯1 3), and (¯1¯1¯3).

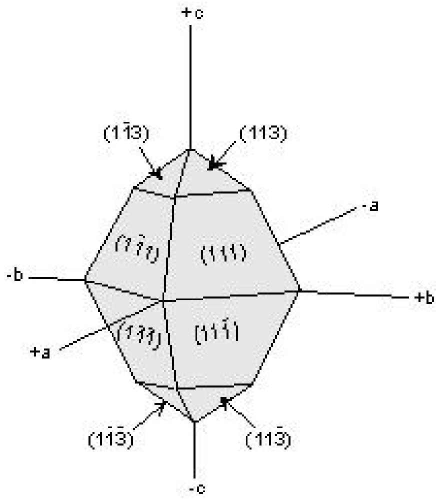


Fig. (49): Illustration of a crystal form.

Such notation is called a form symbol.

An important point to note is that a form refers to a face or set of faces that have the same arrangement of atoms. Thus, the number of faces in a form depends on the symmetry of the crystal.

General Forms and Special Forms

A general form is a form in a particular crystal class that contains faces that intersect all crystallographic axes at different lengths. It has the form symbol {hkl}. All other forms that may be present are called special forms. In the monoclinic, triclinic, and orthorhombic crystal systems, the form {111} is a general form because in these systems faces of this form will intersect the axes a, b, and c at different lengths because the unit lengths are different on each axis. In crystals of higher symmetry, where two or more of the axes have equal length, a general form must intersect the equal length axes at different multiples of the unit length. Thus in the tetragonal system the form {121} is a general form. In the isometric system a general form would have to be something like {123}.

Open Forms and Closed Forms

A closed form is a set of crystal faces that completely enclose space. Thus, in crystal classes that contain closed forms, a crystal can be made up of a single form.

An open form is one or more crystal faces that do not completely enclose space.

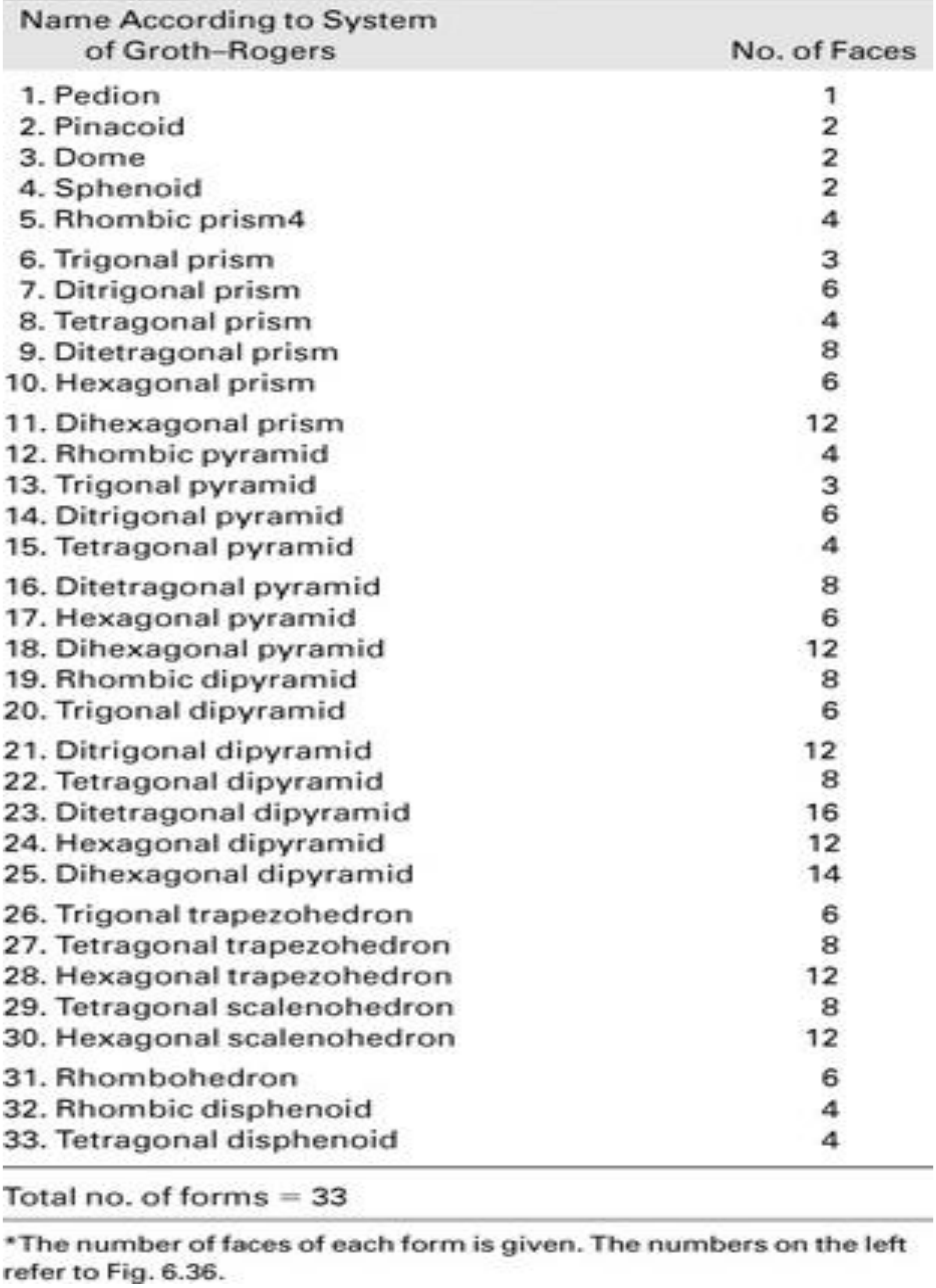
Example 1. Pedions are single faced forms. Since there is only one face in the form a pedion cannot completely enclose space. Thus, a crystal that has only pedions, must have at least 3 different pedions to completely enclose space.

Example 2. A prism is a 3 or more faced form wherein the crystal faces are all parallel to the same line. If the faces are all parallel then they cannot completely enclose space. Thus crystals that have prisms must also have at least one additional form in order to completely enclose space.

Example 3. A dipyramid has at least 6 faces that meet in points at opposite ends of the crystal. These faces can completely enclose space, so a dipyramid is closed form. Although a crystal may be made up of a single dipyramid form, it may also have other forms present.

There are 48 possible forms that can be developed as the result of the 32 combinations of symmetry. We here discuss some, but not all of these forms.

Table (3) Non-isometric crystal forms



Name According to System of Groth–Rogers	No. of Faces
1. Pedion	1
2. Pinacoid	2
3. Dome	2
4. Sphenoid	2
5. Rhombic prism4	4
6. Trigonal prism	3
7. Ditrigonal prism	6
8. Tetragonal prism	4
9. Ditetragonal prism	8
10. Hexagonal prism	6
11. Dihexagonal prism	12
12. Rhombic pyramid	4
13. Trigonal pyramid	3
14. Ditrigonal pyramid	6
15. Tetragonal pyramid	4
16. Ditetragonal pyramid	8
17. Hexagonal pyramid	6
18. Dihexagonal pyramid	12
19. Rhombic dipyramid	8
20. Trigonal dipyramid	6
21. Ditrigonal dipyramid	12
22. Tetragonal dipyramid	8
23. Ditetragonal dipyramid	16
24. Hexagonal dipyramid	12
25. Dihexagonal dipyramid	14
26. Trigonal trapezohedron	6
27. Tetragonal trapezohedron	8
28. Hexagonal trapezohedron	12
29. Tetragonal scalenohedron	8
30. Hexagonal scalenohedron	12
31. Rhombohedron	6
32. Rhombic disphenoid	4
33. Tetragonal disphenoid	4
Total no. of forms = 33	

*The number of faces of each form is given. The numbers on the left refer to Fig. 6.36.

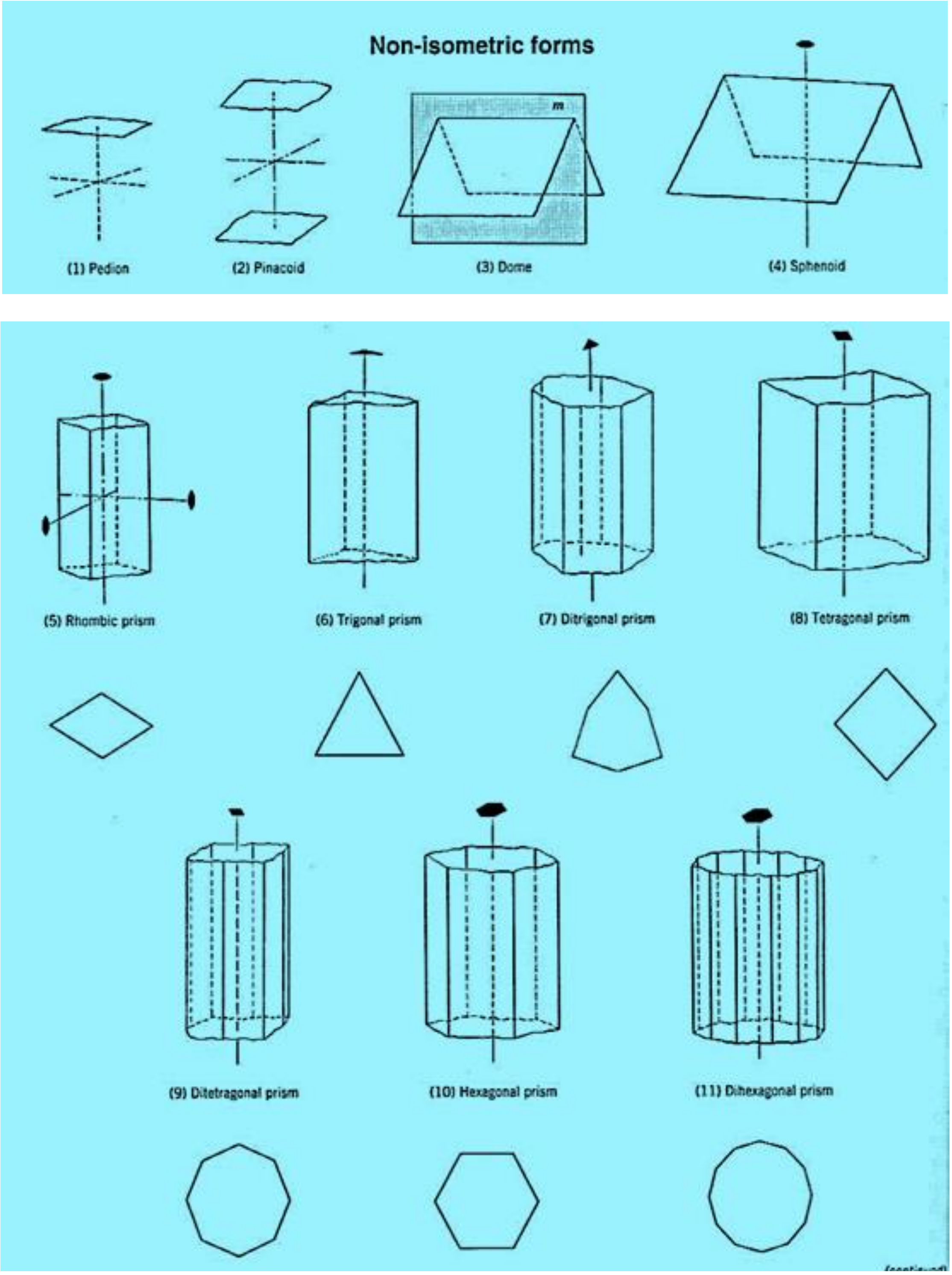
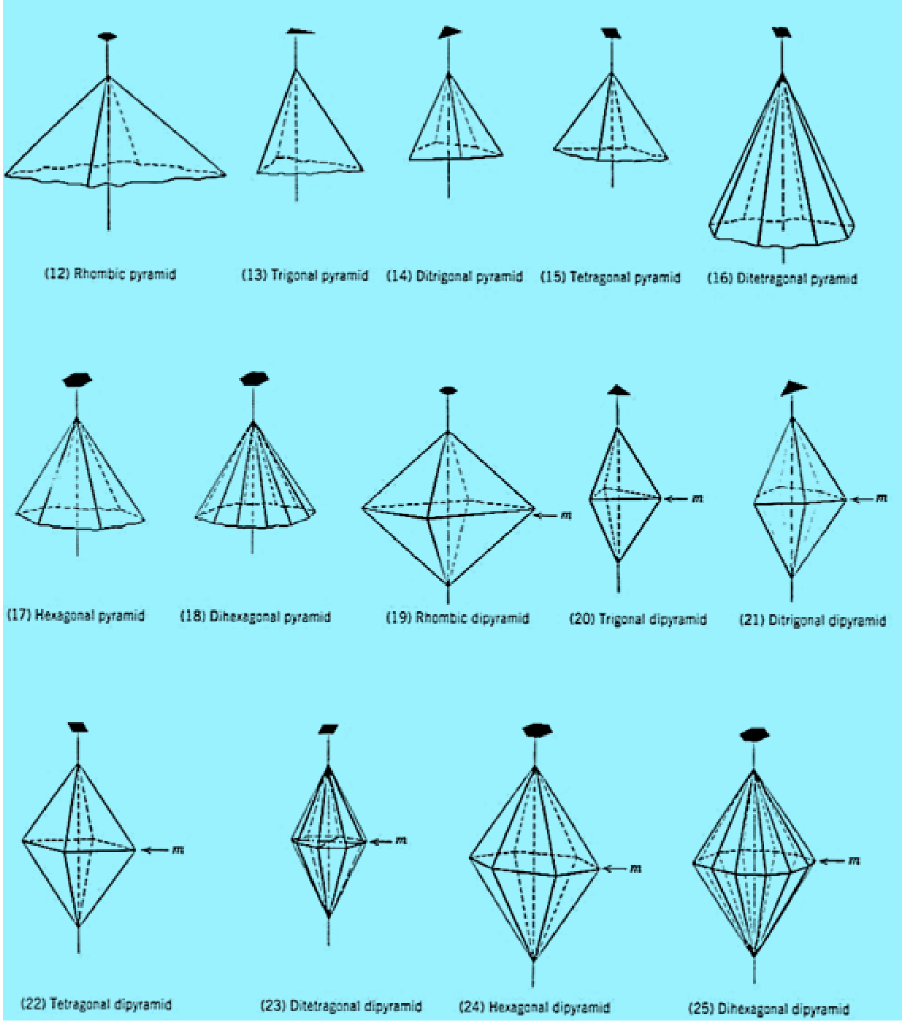
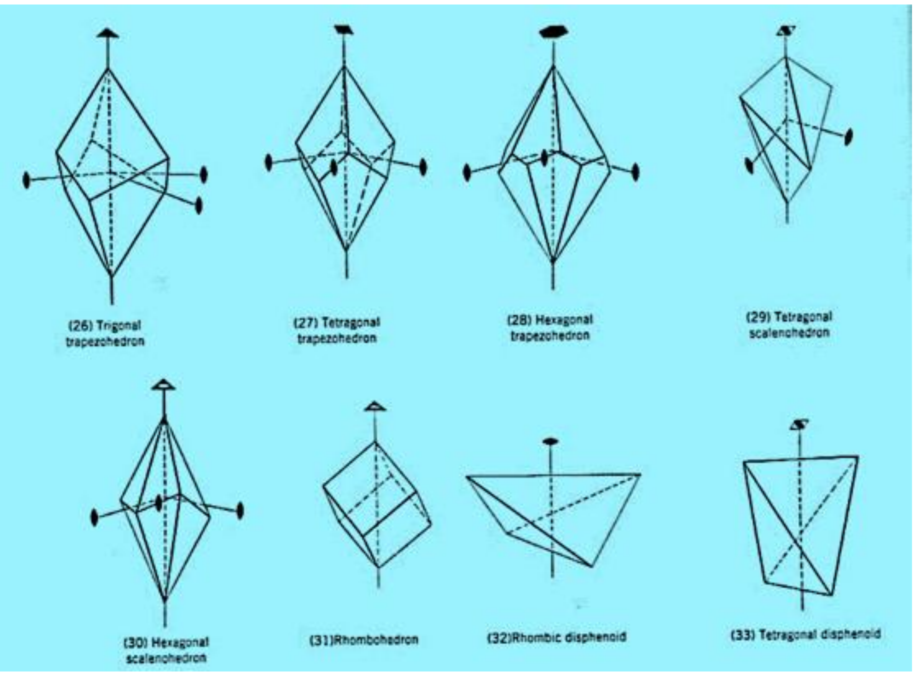


Fig. (50): Non-isometric crystal forms



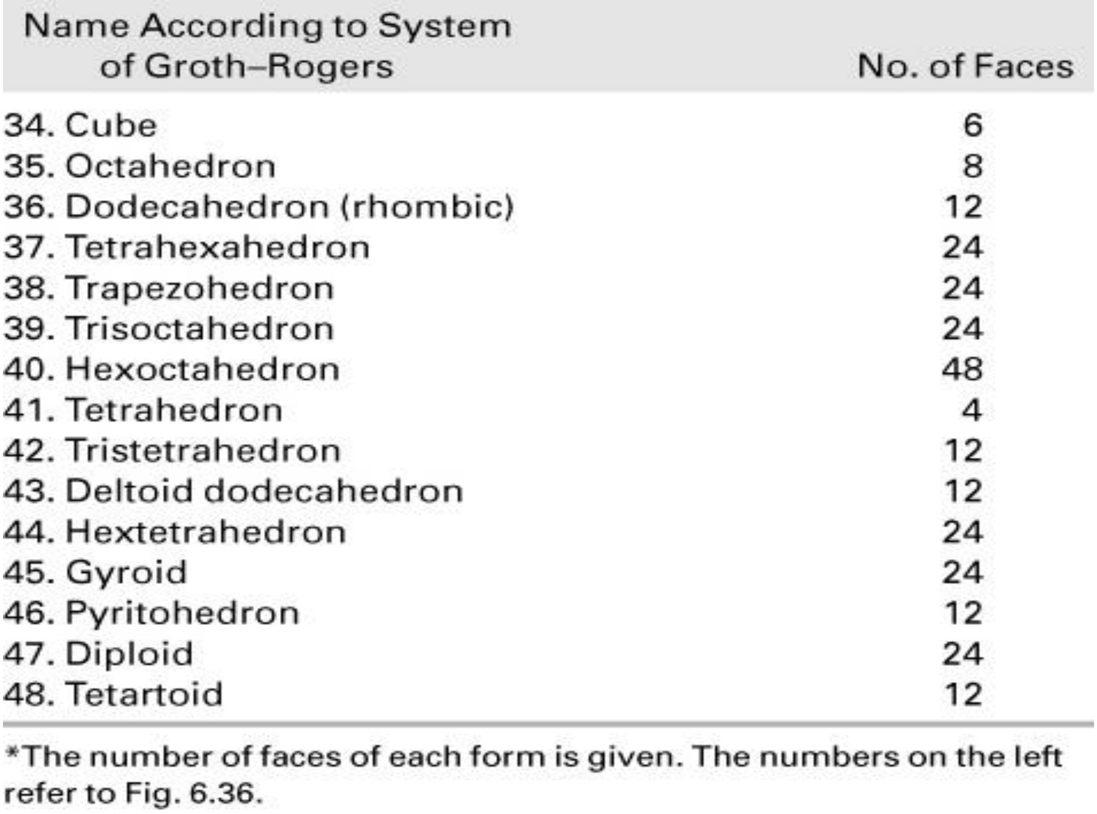
(12) Rhombic pyramid
(13) Trigonal pyramid
(14) Ditrigonal pyramid
(15) Tetragonal pyramid
(16) Ditetragonal pyramid
(17) Hexagonal pyramid
(18) Dihexagonal pyramid
(19) Rhombic dipyramid
(20) Trigonal dipyramid
(21) Ditrigonal dipyramid
(22) Tetragonal dipyramid
(23) Ditetragonal dipyramid
(24) Hexagonal dipyramid
(25) Dihexagonal dipyramid



(26) Trigonal trapezohedron
(27) Tetragonal trapezohedron
(28) Hexagonal trapezohedron
(29) Tetragonal scalenohedron
(30) Hexagonal scalenohedron
(31)Rhombohedron
(32)Rhombic disphenoid
(33) Tetragonal disphenoid

Fig. (50) cont.: Non-isometric crystal forms

Table (4) Isometric crystal forms



Name According to System of Groth–Rogers	No. of Faces
34. Cube	6
35. Octahedron	8
36. Dodecahedron (rhombic)	12
37. Tetrahexahedron	24
38. Trapezohedron	24
39. Trisoctahedron	24
40. Hexoctahedron	48
41. Tetrahedron	4
42. Tristetrahedron	12
43. Deltoid dodecahedron	12
44. Hextetrahedron	24
45. Gyroid	24
46. Pyritohedron	12
47. Diploid	24
48. Tetartoid	12

*The number of faces of each form is given. The numbers on the left refer to Fig. 6.36.

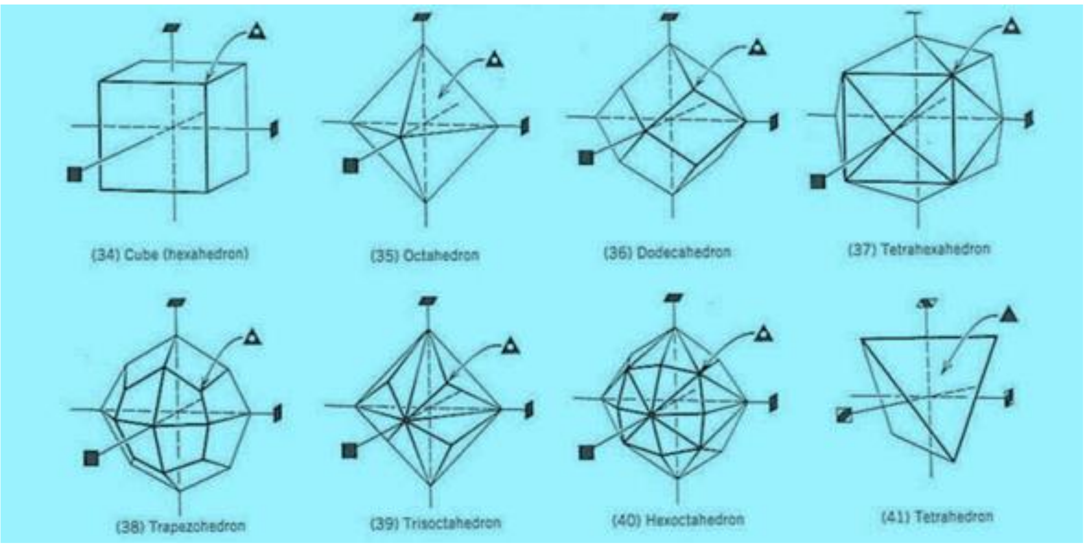


Fig. (51): Isometric crystal forms

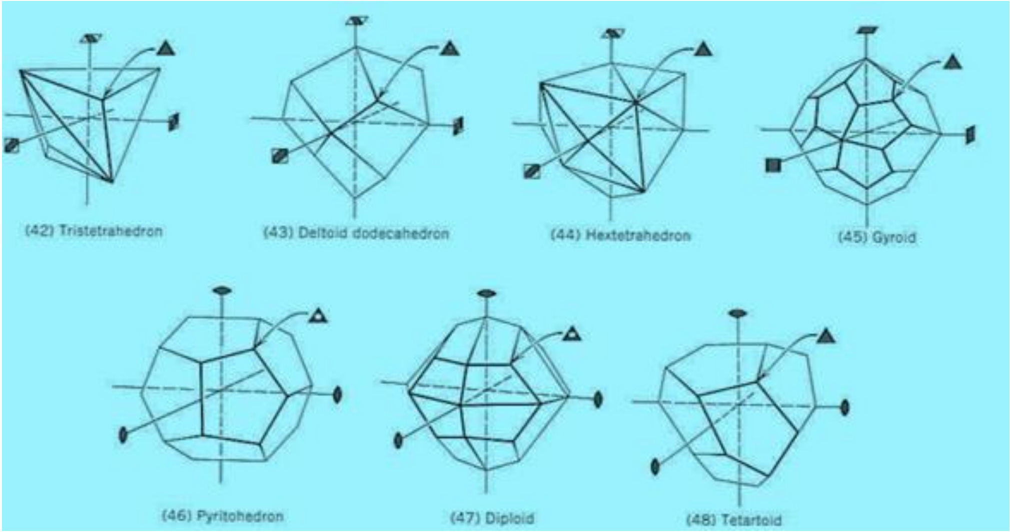
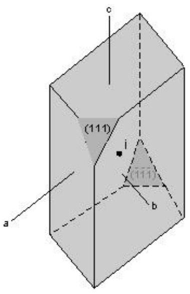
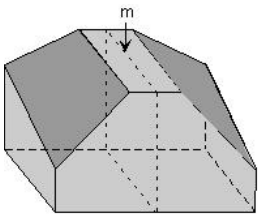
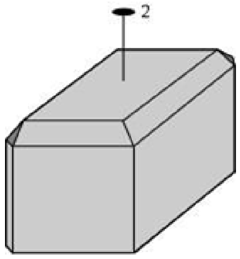
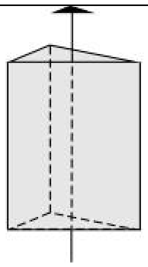
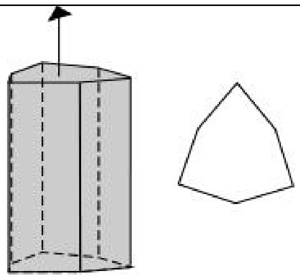
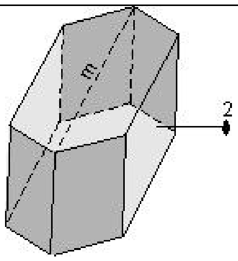
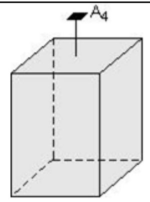
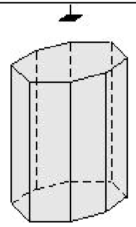
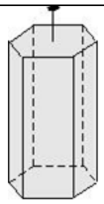
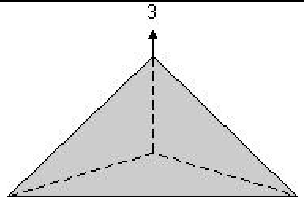
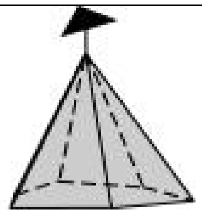
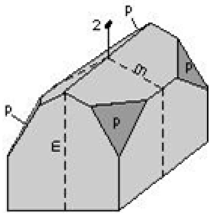


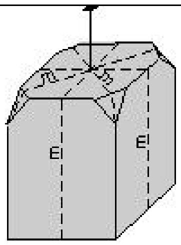
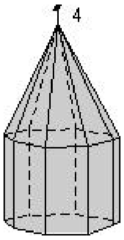
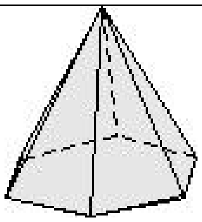
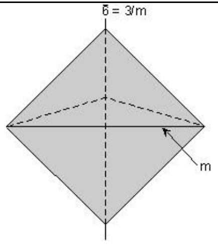
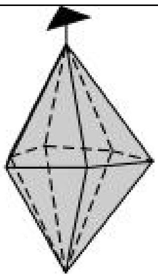
Fig. (51) cont.: Isometric crystal forms

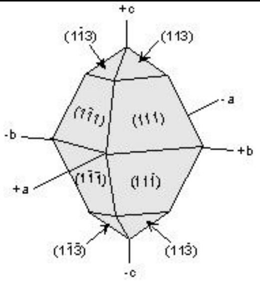
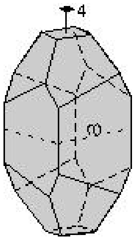
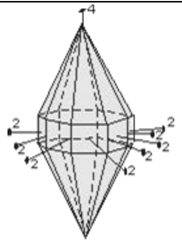
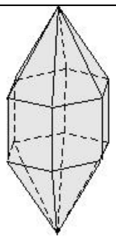
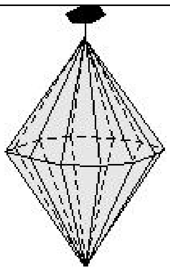
Table (5) Description of crystal forms

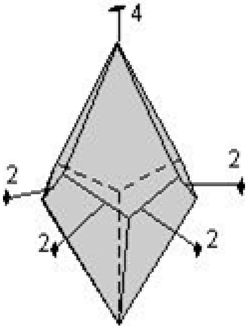
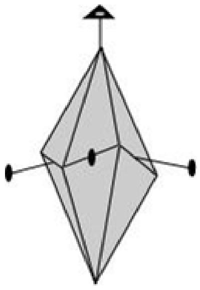
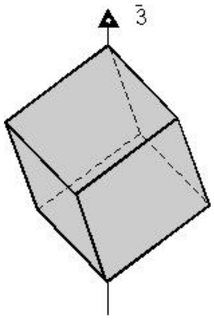
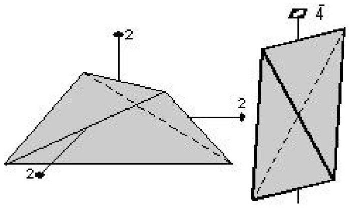
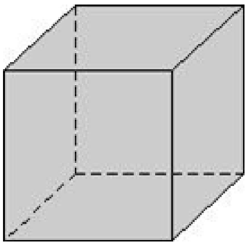
Pedions A pedion is an open, one faced form. Pedions are the only forms that occur in the Pedial class (1). Since a pedion is not related to any other face by symmetry, each form symbol refers to a single face. For example the form {100} refers only to the face (100), and is different from the form $\{\bar{1}00\}$which refers only to the face $(\bar{1}00)$. Note that while forms in the Pedial class are pedions, pedions may occur in other crystal classes.	
Pinacoids A Pinacoid is an open 2-faced form made up of two parallel faces. In the crystal drawing shown here the form {111} is a pinacoid and consists of two faces, (111) and $(\bar{1}\bar{1}\bar{1})$. The form {100} is also a pinacoid consisting of the two faces (100) and $(\bar{1}00)$. Similarly the form {010} is a pinacoid consisting of the two faces (010) and (0-10), and the form {001} is a two faced form consisting of the faces (001) and $(00\bar{1})$. In this case, note that at least three of the above forms are necessary to completely enclose space. While all forms in the Pinacoid class are pinacoids, pinacoids may occur in other crystal classes as well. Domes Domes are 2- faced open forms where the 2 faces are related to one another by a mirror plane. In the crystal model shown here,	 

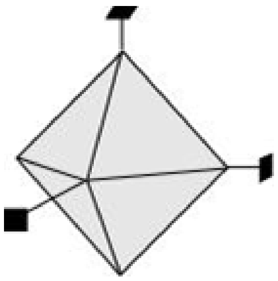
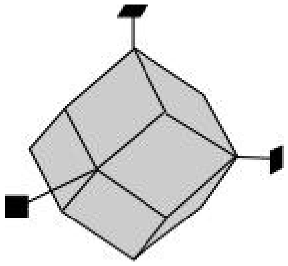
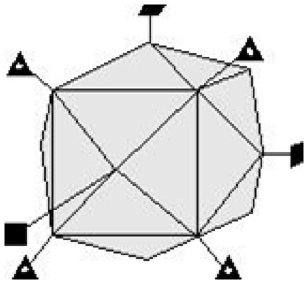
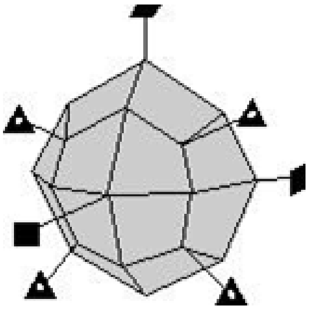
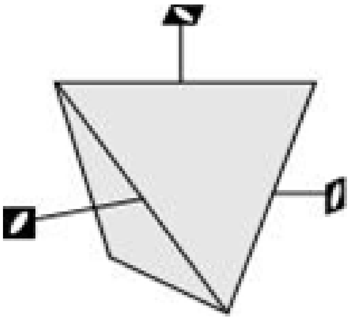
the dark shaded faces belong to a dome. The vertical faces along the side of the model are pinacoids (2 parallel faces). The faces on the front and back of the model are not related to each other by symmetry, and are thus two different pedions.	
Sphenoids Sphenoids are 2 - faced open forms where the faces are related to each other by a 2-fold rotation axis and are not parallel to each other. The dark shaded triangular faces on the model shown here belong to a sphenoid. Pairs of similar vertical faces that cut the edges of the drawing are also pinacoids. The top and bottom faces, however, are two different pedions.	
Prisms A prism is an open form consisting of three or more parallel faces. Depending on the symmetry, several different kinds of prisms are possible. Trigonal prism: 3 - faced form with all faces parallel to a 3 - fold rotation axis	
Ditrigonal prism: 6 - faced form with all 6 faces parallel to a 3-fold rotation axis. Note that the cross section of this form (shown to the right of the drawing) is not a hexagon, i.e. it does not have 6-fold rotational symmetry.	
Rhombic prism: 4 - faced form with all faces parallel to a line that is not a symmetry element. In the drawing to the right, the 4 shaded faces belong to a rhombic prism. The other faces in this model are pinacoids (the faces on the sides belong to a side pinacoid, and the faces on the top and bottom belong to a top/bottom pinacoid).	
Tetragonal prism: 4 - faced open form with all faces parallel to a 4-fold rotation axis or . The 4 side faces in this model make up	

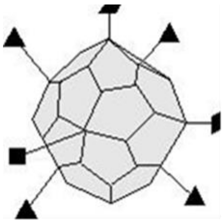
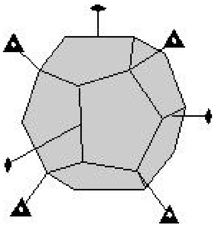
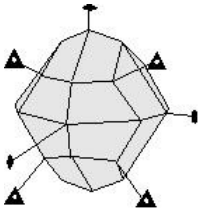
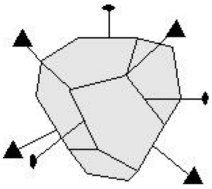
the tetragonal prism. The top and bottom faces make up the a form called the top/bottom pinacoid.	
Ditetragonal prism: 8 - faced form with all faces parallel to a 4-fold rotation axis. In the drawing, the 8 vertical faces make up the ditetragonal prism.	
Hexagonal prism: 6 - faced form with all faces parallel to a 6-fold rotation axis. The 6 vertical faces in the drawing make up the hexagonal prism. Again the faces on top and bottom are the top/bottom pinacoid form.	
Dihexagonal prism: 12 - faced form with all faces parallel to a 6-fold rotation axis. Note that a horizontal cross-section of this model would have apparent 12-fold rotation symmetry. The dihexagonal prism is the result of mirror planes parallel to the 6-fold rotation axis.	
Pyramids A pyramid is a 3, 4, 6, 8 or 12 faced open form where all faces in the form meet, or could meet if extended, at a point. Trigonal pyramid: 3-faced form where all faces are related by a 3-fold rotation axis.	
Ditrigonal pyramid: 6-faced form where all faces are related by a 3-fold rotation axis. Note that if viewed from above, the ditrigonal pyramid would not have a hexagonal shape; its cross section would look more like that of the trigonal prism discussed above.	
Rhombic pyramid: 4-faced form where the faces are related by mirror planes. In the drawing shown here the faces labeled "p" are the four faces of the rhombic pyramid. If extend, these 4 faces would meet at a point.	

Tetragonal pyramid: 4-faced form where the faces are related by a 4 axis. In the drawing the small triangular faces that cut the corners represent the tetragonal pyramid. Note that if extended, these 4 faces would meet at a point.	
Ditetragonal pyramid: 8-faced form where all faces are related by a 4 axis. In the drawing shown here, the upper 8 faces belong to the ditetragonal pyramid form. Note that the vertical faces belong to the ditetragonal prism.	
Hexagonal pyramid: 6-faced form where all faces are related by a 6 axis. If viewed from above, the hexagonal pyramid would have a hexagonal shape.	
Dihexagonal pyramid: 12-faced form where all faces are related by a 6-fold axis. This form results from mirror planes that are parallel to the 6-fold axis.	
Dipyramids Dipyramids are closed forms consisting of 6, 8, 12, 16, or 24 faces. Dipyramids are pyramids that are reflected across a mirror plane. Thus, they occur in crystal classes that have a mirror plane perpendicular to a rotation or rotoinversion axis. Trigonal dipyramid: 6-faced form with faces related by a 3-fold axis with a perpendicular mirror plane. In this drawing, all six faces belong to the trigonal-dipyramid.	
Ditrigonal-dipyramid: 12-faced form with faces related by a 3-fold axis with a perpendicular mirror plane. If viewed from above, the crystal will not have a hexagonal shape; rather it would appear similar to the horizontal cross-section of the ditrigonal prism, discussed above.	

Rhombic dipyramid: 8-faced form with faces related by a combinations of 2-fold axes and mirror planes. The drawing to the right shows 2 rhombic dipyramids. One has the form symbol {111} and consists of the four larger faces shown plus four equivalent faces on the back of the model. The other one has the form symbol {113} and consists of the 4 smaller faces shown plus the four on the back.	
Tetragonal dipyramid: 8-faced form with faces related by a 4-fold axis with a perpendicular mirror plane. The drawing shows the 8-faced tetragonal dipyramid. Also shown is the 4-faced tetragonal prism, and the 2-faced top/bottom pinacoid.	
Ditetragonal-dipyramid: 16-faced form with faces related by a 4-fold axis with a perpendicular mirror plane. The ditetragonal-dipyramid is shown here. Note the vertical faces belong to a ditetragonal prism.	
Hexagonal dipyramid: 12-faced form with faces related by a 6-fold axis with a perpendicular mirror plane. The vertical faces in this model make up a hexagonal prism.	
Dihexagonal-dipyramid: 24-faced form with faces related by a 6-fold axis with a perpendicular mirror plane.	

Trapezohedrons Trapezohedron are closed 6, 8, or 12 faced forms, with 3, 4, or 6 upper faces offset from 3, 4, or 6 lower faces. The trapezohedron results from 3-, 4-, or 6-fold axes combined with a perpendicular 2-fold axis. An example of a tetragonal trapezohedron is shown in the drawing to the right. Other examples are shown in your textbook.	
Scalenohedrons A scalenohedron is a closed form with 8 or 12 faces. In ideally developed faces each of the faces is a scalene triangle. In the model, note the presence of the 3-fold rotoinversion axis perpendicular to the 3 2-fold axes.	
Rhombohedrons A rhombohedron is 6-faced closed form wherein 3 faces on top are offset by 3 identical upside down faces on the bottom, as a result of a 3-fold rotoinversion axis. Rhombohedrons can also result from a 3-fold axis with perpendicular 2-fold axes. Rhombohedrons only occur in the crystal classes 2/m , 32, and .	
Disphenoids A disphenoid is a closed form consisting of 4 faces. These are only present in the orthorhombic system (class 222) and the tetragonal system (class) The rest of the forms all occur in the isometric system, and thus have either four 3-fold axes or four axes. Only some of the more common isometric forms will be discussed here.	
Hexahedron A hexahedron is the same as a cube. 3-fold axes are perpendicular to the face of the cube, and four axes run through the corners of the cube. Note that the form symbol for a hexahedron is {100}, and it consists of the following 6 faces:(100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$.).	

Octahedron An octahedron is an 8 faced form that results from three 4-fold axes with perpendicular mirror planes. The octahedron has the form symbol {111} and consists of the following 8 faces: (111), $(\bar{1}\bar{1}\bar{1})$, $(1\bar{1}1)$, $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, $(11\bar{1})$, and $(\bar{1}11)$. . Note that four 3-fold axes are present that are perpendicular to the triangular faces of the octahedron.	
Dodecahedron A dodecahedron is a closed 12-faced form. Dodecahedrons can be formed by cutting off the edges of a cube. The form symbol for a dodecahedron is {110}. As an exercise, you figure out the Miller Indices for these 12 faces.	
Tetrahexahedron The tetrahexahedron is a 24-faced form with a general form symbol of {0hl}. This means that all faces are parallel to one of the a axes, and intersect the other 2 axes at different lengths.	
Icositetrahedron (Trapezohedron) An isometric trapezohedron is a 12-faced closed form with the general form symbol {hhl}. This means that all faces intersect two of the a axes at equal length and intersect the third a axis at a different length.	
Tetrahedron The tetrahedron occurs in the class $\bar{4}3m$ and has the form symbol {111} (the form shown in the drawing) or $\{1\bar{1}1\}$ (2 different forms are possible). It is a four faced form that results from three $\bar{4}$ axes and four 3-fold axes (not shown in the drawing).	

Gyroid A gyroid is a form in the class 432 (note no mirror planes)	
Pyritohedron A 12-faced form that occurs in the crystal class 2/m. Note that there are no 4-fold axes in this class. The possible forms are {h0l} or {0kl} and each of the faces that make up the form have 5 sides.	
Diploid The diploid is the general form {hkl} for the diploidal class (2/m). Again there are no 4-fold axes.	
Tetartoid Tetartoids are general forms in the tetartoidal class (23) which only has 3-fold axes and 2-fold axes with no mirror planes.	

Understanding Miller Indices, Form Symbols, and Forms

In class we will fill in the following table in order to help you better understand the relationship between form and crystal faces. The assignment will be to determine for each form listed across the top of the table the number of faces in that form, the name of the form, and the number of cleavage directions that the form symbol would imply for each of the crystal classes listed in the left-hand column.

Before we can do this, however, we need to review how we define the crystallographic axes in relation to the elements of symmetry in each of the crystal systems.

Triclinic - Since this class has such low symmetry there are no constraints on the axes, but the most pronounced face should be taken as parallel to the c axis.

Monoclinic - The 2 fold axis is the b axis, or if only a mirror plane is present, the b axis is perpendicular to the mirror plane.

Orthorhombic - The current convention is to take the longest axis as b, the intermediate axis is a, and the shortest axis is c. An older convention was to take the c axis as the longest, the b axis intermediate, and the a axis as the shortest.

Tetragonal - The c axis is either the 4 fold rotation axis or the rotoinversion axis.

Hexagonal - The c axis is the 6-fold, 3-fold, axis, or.

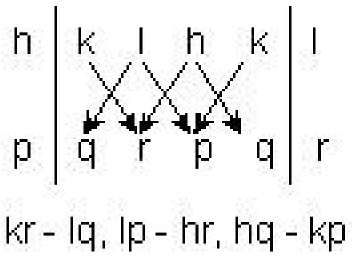
Isometric - The equal length a axes are either the 3 4-fold rotation axes, rotoinversion axes, or, in cases where no 4 or axes are present, the 3 2-fold axes.

Zones and Zone Symbols

A zone is defined as a group of crystal faces that intersect in parallel edges. Since the edges will all be parallel to a line, we can define that the direction of the line using a notation similar to Miller Indices. This notation is called the zone symbol. The zone symbol looks like a Miller Index, but is enclosed in square brackets, i.e. [uvw].

For a group of faces in the same zone, we can determine the zone symbol for all non-hexagonal minerals by choosing 2 non-parallel faces (hkl) and (pqr).

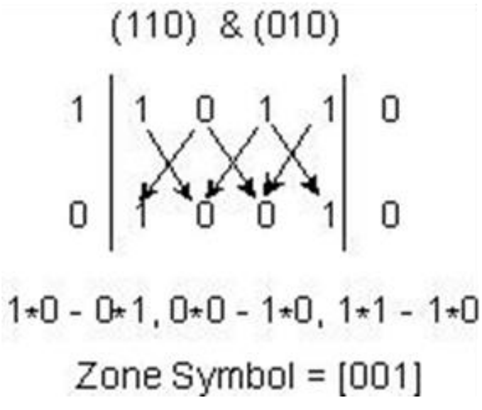
To do so, we write the Miller Index for each face twice, one face directly beneath the other, as shown below. The first and last numbers in each line are discarded. Then we apply the following formula to determine the indices in the zone symbol.



u = k*r - l*q, v = l*p - h*r, and w = h*q - k*p

For example, faces (110) and (010) are not parallel to each other.

The zone symbol for these faces (and any other faces that lie in the same zone) is determined by writing 110 twice and then immediately below, writing 010 twice. Applying the formula above gives the zone symbol for this zone as [001].



Note that this zone symbol implies a line that is perpendicular to the face with the same index. In other words, [001] is a line perpendicular to the face (001). It can thus be used as a symbol for a line. In this case, the line is the c crystallographic axis.

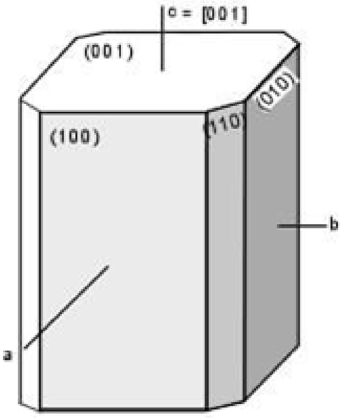


Fig. (52): Crystal Zone and Zone Axis.

Zone symbols, therefore are often used to denote directions through crystals. Being able to specify directions in crystals is important because many properties of minerals depend on direction. These are called vectorial properties.

Crystal Habit

The term "crystal habit" is used to identify the shape, size and appearance of a crystal's unique growth characteristics, or "Crystal Forms". Crystal habits are useful in communicating what specimens of a particular mineral would, or should look like. There are approximately 36 standardized terms to describe the variations, or habits of crystal growth. A particular mineral may exhibit several different habits, all of which are influenced by the following factors:

1. Crystal Twinning (two individual crystals share some of the same crystal lattice points)
2. Growth Conditions (heat, pressure, and space)
3. Trace Impurities (present during crystal formation)

When one mineral replaces another while preserving the original mineral's growth habit it is called a "pseudomorphous replacement. Most gemstone crystals are not found as perfectly formed single crystals but are found as aggregates of several crystals grown together in one mass.

Table (6) Common Crystal Habits

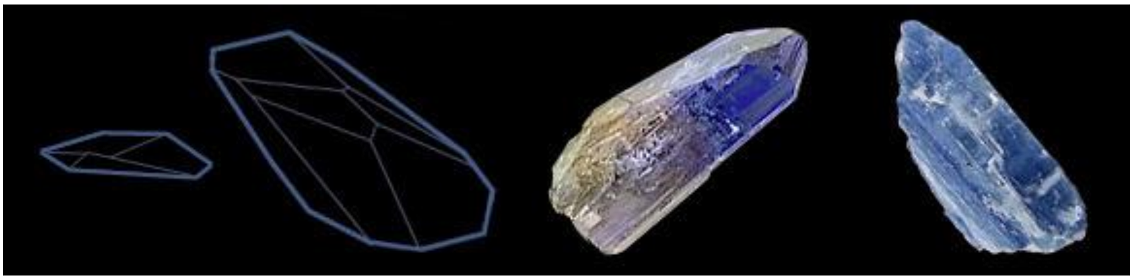
Crystal Habit:	Habit Description:	Mineral:
Acicular	Needle-like, slender and/or tapered	Rutile (Quartz)
Anhedral	Poorly formed and distorted	Olivine

Banded	narrow bands of differing colors	Onyx
Bladed	Slender, flattened and blade-like	Tanzanite
Columnar	Long, slender prisms and parallel growth	Calcite
Dendritic	Tree-like multi-directional branching from central point	Opal
Dodecahedral	12-sided Dodecahedron	Garnet
Drusy (Encrustation)	Aggregate of minute crystals coating a surface	Drusy (Quartz)
Enantiomorphic	Mirror-image (left/right) habit and optical characteristics	Citrine, Amethyst
Equant (Stubby)	Squashed, pinnacoids dominant over prisms	Zircon
Euhedral	Well-formed and Undistorted	Spinel
Foliated	Easily separated into plates	Mica
Geode	Rock cavities with internal crystals & encrustation	Amethyst, Quartz
Granular Mass	Anhedral crystals in lumpy mass with no crystal form	Peridot
Mamillary	Intersecting large rounded contours	Malachite
Massive	Shapeless with no distinct external crystal shape	Lapis Lazuli
Octahedral	Eight-sided octahedron - two pyramids, base to base	Diamond
Pincoid	Terminated by multiple pyramidal faces	Emerald, Beryl
Prismatic	Elongate and Prism-Like, all faces are	Tourmaline,

	parallel to c-axis	Topaz
Pseudomorphous	Occurring in the shape of another mineral	Tiger's Eye
Striated	Surface growth lines parallel or perpendicular to c-axis	Alexandrite
Tabular (Lamellar)	Flat, tablet-shaped, prominent pinnacoid	Ruby

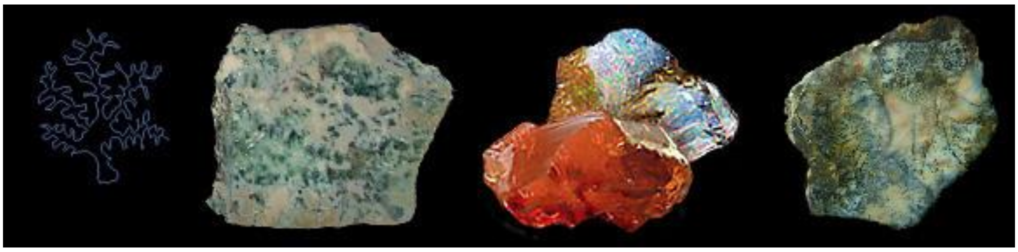
Acicular Crystal Habit: Three variations of Acicular Rutilated Quartz

2. Bladed Crystal Habit: Bladed Tanzanite (center) and Kyanite (right)

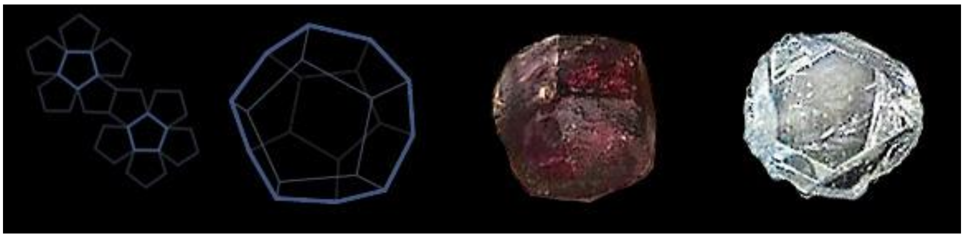


3. Columnar Crystal Habit: Columnar Quartz (left), Smoky Quartz (center), and Basalt Rock (Yellowstone, Wyoming) Formations (right).

4. Dendritic Crystal Habit: Dendritic Agate (left), Opal (center), and Agate (right)



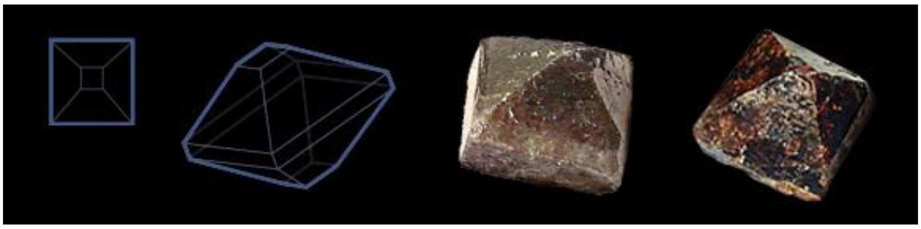
5. Dodecahedral Crystal Habit: Dodecahedral Garnet (center), Diamond Rough (right)



6. Drusy Crystal Habit : Three variations of Druzy Quartz

7. Enantiomorphic Crystal Habit: Enantiomorphic ("Japan Law" or "Left-Right" Twins) Quartz (center), Amethyst (right).

8. Equant Crystal Habit: Equant Zircon Roughs (center, and right)

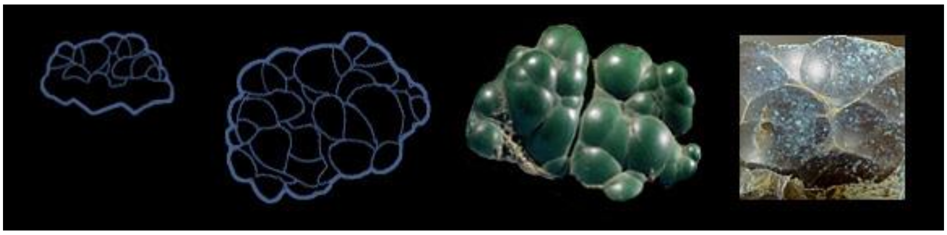


9. Euhedral Crystal Habit: Euhedral (Octahedral) Red Spinel (center, and right)

10. Geode Crystal Habit: Uncut Geode (left), Amethyst Geode (center), and Quartz Geode (right)

11. Granular Mass Habit: Granular Mass Peridot (center), and Peridotite Encrustation (right)

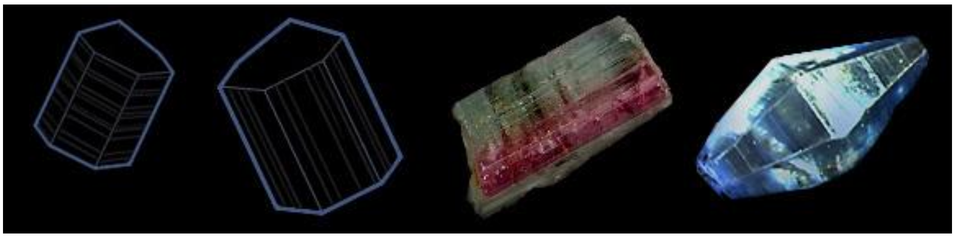
12. Mamillary Crystal Habit: Mamillary Malachite (center), and Chalcedony (right)



13. Octahedral Crystal: Octahedral White Spinel (center), Diamond Rough (right)Habit

14. Pincoid Crystal Habit : Pincoid (Prismatic) Aquamarine (center), Emerald (right)

15. Striated Crystal Habit : Striated (Prismatic) Tourmaline (center), Striated Sapphire (right)



16. Tabular Crystal Habit: Tabular Calcite (center), Ruby (right)

Fig. (53): Common Crystal Habits.

Twinning in Crystals

Sometimes during the growth of a crystal, or if the crystal is subjected to stress or temperature/pressure conditions different from those under which it originally formed, two or more intergrown crystals are formed in a symmetrical fashion. These symmetrical intergrowths of crystals are called twinned crystals. Twinning is important to recognize, because when it occurs, it is often one of the most diagnostic features enabling identification of the mineral.

What happens is that lattice points in one crystal are shared as lattice points in another crystal adding apparent symmetry to the crystal pairs. Twinning, because it adds symmetry, never occurs in relation to the existing symmetry of the crystal.

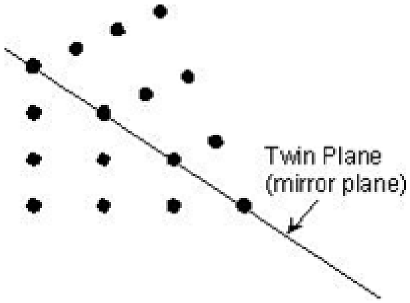


Fig. (54): Crystal lattice in a twin and the mirror plane.

Symmetry Operations that Define Twinning

Because symmetry is added to a crystal by twinning, twining can be defined by the symmetry operations that are involved. These include:

-Reflection across a mirror plane. The added mirror plane would then be called a twin plane.

-Rotation about an axis or line in the crystal. The added rotation axis would then be called a twin axis.

-Inversion through a point. The added center of symmetry would then be called a twin center.

Twin Laws

Twin laws are expressed as either form symbols to define twin planes (i.e. {hkl}) or zone symbols to define the direction of twin axes (i.e. [hkl]).

The surface along which the lattice points are shared in twinned crystals is called a composition surface.

If the twin law can be defined by a simple planar composition surface, the twin plane is always parallel to a possible crystal face and never parallel to an existing plane of symmetry (remember that twinning adds symmetry).

If the twin law is a rotation axis, the composition surface will be irregular, the twin axis will be perpendicular to a lattice plane, but will never be an even-fold rotation axis of the existing symmetry. For example twinning cannot occur on a new 2 fold axis that is parallel to an existing 4-fold axis.

Types of Twinning

Another way of defining twinning breaks twins into two separate types.

Contact Twins - have a planar composition surface separating 2 individual crystals. These are usually defined by a twin law that expresses a twin plane (i.e. an added mirror plane). An example shown here is a crystal of orthoclase twinned on the Braveno Law, with {021} as the twin plane.

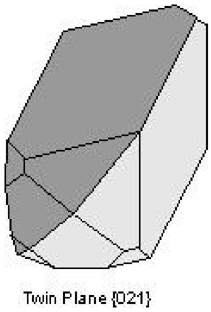


Fig. (55): Contact Twin of orthoclase crystal (Braveno Law).

Penetration Twins - have an irregular composition surface separating 2 individual crystals. These are defined by a twin center or twin axis. Shown here is a twinned crystal of orthoclase twinned on the Carlsbad Law with [001] as the twin axis.

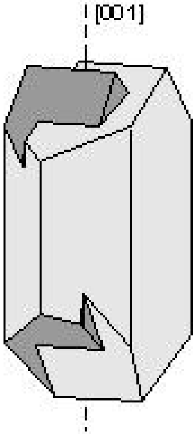


Fig. (56): Penetration Twin of orthoclase crystal (Carlsbad Law).

Contact twins can also occur as repeated or multiple twins.

-If the compositions surfaces are parallel to one another, they are called polysynthetic twins. Plagioclase commonly shows this type of twinning, called the Albite Twin Law, with {010} as the twin plane. Such twinning is one of the most diagnostic features of plagioclase.

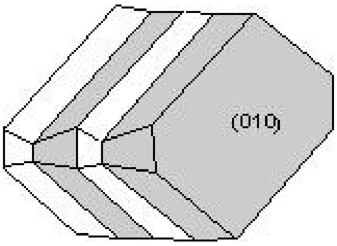


Fig. (57): Multiple Twin (polysynthetic Twin) of Albite crystal (Albite Law).

-If the composition surfaces are not parallel to one another, they are called cyclical twins. Shown here is the cyclical twin that occurs in chrysoberyl along a {031} plane.

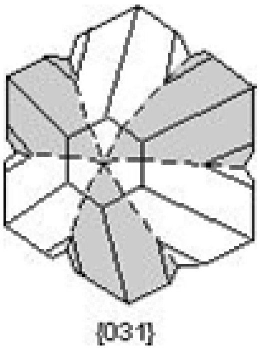


Fig. (58): Multiple Twin (Cyclical Twin) chrysoberyl crystal.

Origin of Twinning

Twinning can originate in 3 different ways, as growth twins, transformation twins, and glide or deformation twins.

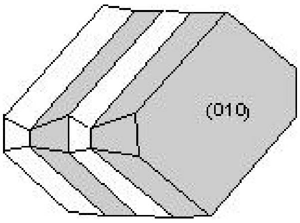
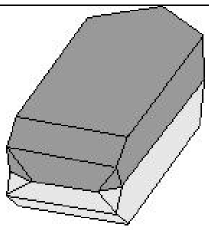
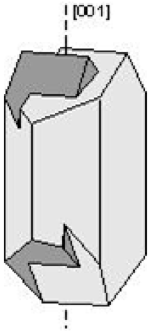
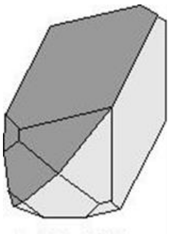
1.Growth Twins - When accidents occur during crystal growth and a new crystal is added to the face of an already existing crystal, twinning can occur if the new crystal shares lattice points on the face of the existing crystal, but has an orientation different from the original crystal. Such growth twins can be contact twins, as illustrated here, or can be penetration twins. All of twins discussed so far are growth twins.

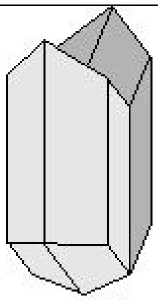
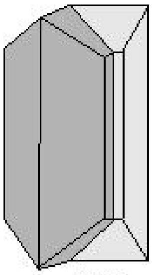
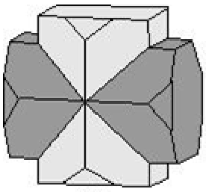
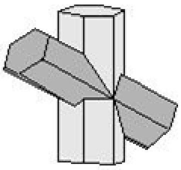
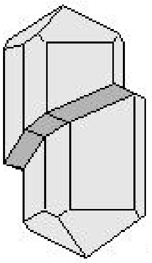
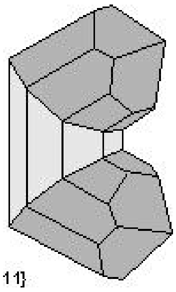
2. Transformation Twins - Transformation twinning occurs when a preexisting crystal undergoes a transformation due to a change in pressure or temperature. This commonly occurs in minerals that have different crystal structures and different symmetry at different temperatures or pressures. When the temperature or pressure is changed to that where a new crystal structure and symmetry is stable, different parts of the crystal become arranged in different symmetrical orientations, and thus form an intergrowth of one or more crystals. Dauphiné and Brazil twinning in quartz commonly forms this way during a decrease in temperature.

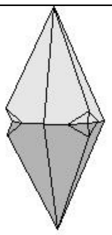
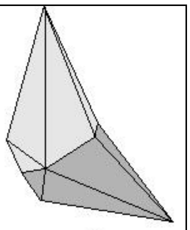
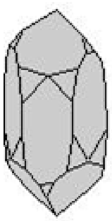
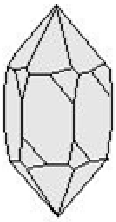
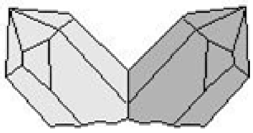
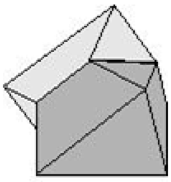
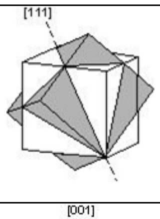
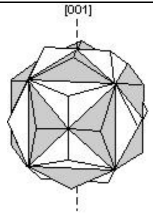
Similarly the combination of albite twinning and pericline winning in alkali feldspar results when high temperature sanidine (monoclinic) transforms to low temperature microcline (triclinic). This type of twinning is only observed using the polarizing microscope, and results in a "tartan" twinning pattern as shown in your text book on page 231, figure10.18. When this twinning pattern is observed with the microscope it is one of the most characteristic diagnostic properties for the identification of microcline.

3. Deformation Twins - During deformation atoms can be pushed out of place. If this happens to produce a symmetrical arrangement, it produces deformation twins. The mineral calcite can be easily twinned in this way, producing polysynthetic twins on {01 2}.

Table (7) Common Twin Laws

Triclinic System - The feldspar minerals plagioclase and microcline are the most common triclinic minerals that show twinning. Two common twin laws are observed in these feldspars. Albite Law - As described above, plagioclase (NaAlSi3O8 - CaAl2Si2O8) very commonly shows albite polysynthetic twinning. The twin law - {010} indicates that the twining occurs perpendicular to the b crystallographic axis. Albite twinning is so common in plagioclase, that its presence is a diagnostic property for identification of plagioclase. Pericline Law - The pericline law has [010] as the twin axis. As stated above, pericline twinning occurs as the result of monoclinic orthoclase or sanidine transforming to microcline (all have the same chemical formula - KAlSi3O8). Pericline twinning usually occurs in combination with albite twinning in microcline, but is only observable with the polarizing microscope. The combination of pericline and albite twinning produce a cross-hatched pattern, called tartan twinning, as discussed above, that easily distinguishes microcline from the other feldspars under the microscope.	
Monoclinic System - The most common twins in the monoclinic system occur on the planes {100} and {001}. The feldspars - orthoclase and sanidine - are the most commonly twinned minerals in the monoclinic system. Both contact twins and penetration twins occur, and both types result from accidents during growth. Manebach Law - {001} - forms a contact twin commonly observed in the mineral orthoclase. This twinning is very diagnostic of orthoclase when it occurs. Carlsbad Law - [001] - forms a penetration twin in the mineral orthoclase. Crystals twinned under the Carlsbad Law show two intergrown crystals, one rotated 180o from the other about the [001] axis. Carlsbad twinning is the most common type of twinning in orthoclase, and is thus very diagnostic of orthoclase when it occurs. Braveno Law - {021} - forms a contact twin in the mineral orthoclase.	 Twin Plane {001}   Twin Plane {021}

Swallow Tail Twins - {100}- are commonly observed in the mineral gypsum ($CaSO4.2H2O$).	
Orthorhombic System - Orthorhombic crystals commonly twin on planes parallel to a prism face. The most common is a {110} twin that results in many orthorhombic minerals having cyclical twins. {110} Cyclical Twins - The mineral aragonite ($CaCO3$) , chrysoberyl ($BeAl2O4$), and cerrusite ($PbCO3$) commonly develop twinning on {110}. This results in a cyclical twin which gives these minerals a pseudo-hexagonal appearance.	
Staurolite Law - The mineral staurolite is really monoclinic, but it has a ß angle very close to 90o so it has the appearance of an orthorhombic mineral. Two types of interpenetration twins occur in staurolite the {031} twins from a right-angled cross and the {231} twins form a cross at about 60o.	 
Tetragonal System - Twinning in the tetragonal system usually occurs on {011} forming cyclical contact twins. The minerals rutile ($TiO2$) and cassiterite ($SnO2$) commonly show this type of twinning.	  {011}

Hexagonal System - The minerals calcite (CaCO3) and quartz (SiO2) are the most common hexagonal minerals and both show the types of twinning common in hexagonal minerals. Calcite Twins - The two most common twin laws that are observed in calcite crystals are {0001} and the rhombohedron {01 2}. Both are contact twins, but the {01 2} twins can also occur as polysynthetic twins that result from deformation. Quartz shows three other hexagonal twins. Brazil Law - {11 0} - is a penetration twin that results from transformation. Dauphiné Law - [0001] - is also a penetration twin that results from transformation. Japanese Law - {11 2} - is a contact twin that results from accidents during growth.	 {0001}  {01$\bar{1}$2}  Brazil Twin {11$\bar{2}$0}  Dauphine Twin [0001]  Japanese Twin {11$\bar{2}$2}
Isometric System - Three types of twins are common in the isometric system. Spinel Law - $\{\bar{1}\bar{1}1\}$- is a twin plane, parallel to an octahedron. It occurs commonly in mineral spinel (MgAl2O4).	 {$\bar{1}\bar{1}$1}
[111] - The twin axis perpendicular to an octahedral face adds three fold rotational symmetry.	
Iron Cross [001] - The mineral pyrite (FeS2) often shows the iron cross made of the interpenetration of two pyritohedrons. Since this occurs in the class 2/m , with no 4-fold rotation axes, the [001] twin axis gives the mineral apparent 4-fold symmetry about 3 perpendicular axes.	

Crystal Faces Projection

First we define the interfacial angle between two crystal faces as the angle between lines that are perpendicular to the faces. Such lines are called the poles to the crystal face. Note that this angle is can be measured easily with a device called a contact goniometer.

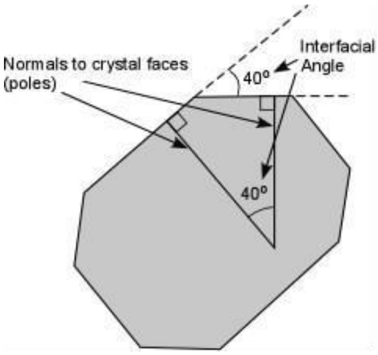


Fig. (59): Measuring interfacial angle between two crystal faces.

Next, we need a systematic way to define crystallographic angles. For this we use a spherical projection.

spherical projection

Imagine that we have a crystal inside of a sphere. From each crystal face we draw a line perpendicular to the face (poles to the face).

The pole to a hypothetical (010) face will coincide with the b crystallographic axis, and will impinge on the inside of the sphere at the equator.

We define this face (010) as having a φ angle of 0^o. For any other face, the φ angle will be measured from the b axis in a clockwise sense in the plane of the equator.

We define the ρ angle, as the angle between the c axis and the pole to the crystal face, measured downward from the North Pole of the sphere.

In the diagram shown here, a crystal face has a ρ angle measured in the vertical plane containing the axis of the sphere and the face pole, and a φ angle measured in the horizontal equatorial plane. Note that the (010) face has a ρ angle = 90^o.

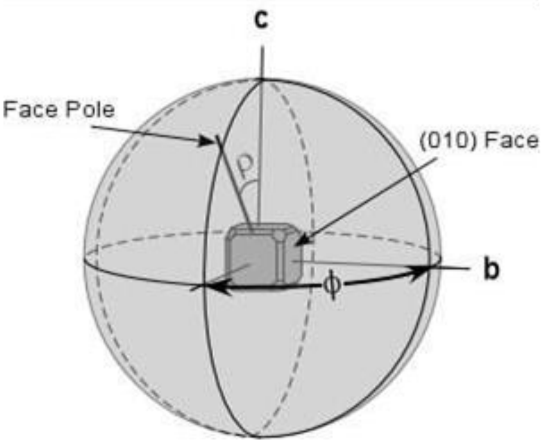


Fig. (60): Spherical projection of crystal faces.

Note that these angular measurements are similar to those we use for latitude and longitude to plot positions of points on the Earth's surface. For the Earth, longitude is similar to the φ angle, except longitude is measured from the Greenwich Meridian, defined as φ = 0°. Latitude is measured in the vertical plane, up from the equator, shown as the angle θ. Thus, the ρ angle is what is called the colatitude (90° - latitude).

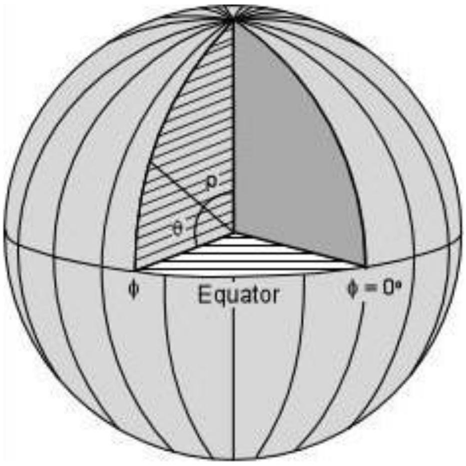


Fig. (61): Illustration of ρ and φ angles .

As an example, the ρ and φ angles for the (111) crystal face in a crystal model is shown here. Note again that the ρ angle is measured in the vertical plane containing the c axis and the pole to the face, and the φ angle is measured in the horizontal plane, clockwise from the b axis.

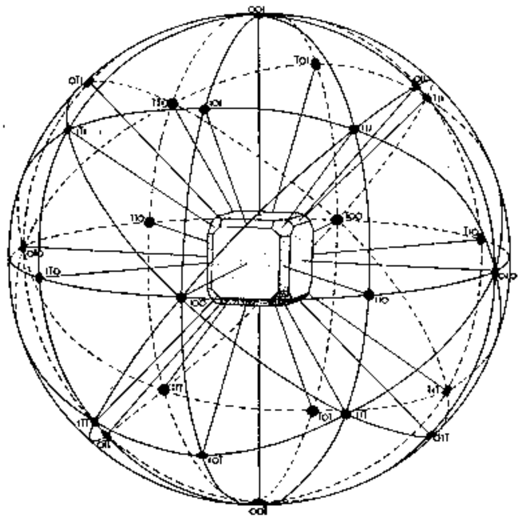


Fig. (62): The spherical projection of a crystal .

Generally, it is the angles of the spherical projection, ρ and φ, that are given for each face of a crystal. If these are known, then the actual angles between any two faces can easily be obtained through trigonometry, or by use of the stereonet as discussed below.

Remember that it is the angular relationships between crystal faces that actually reflect the ordered internal arrangement of atoms and thus the internal symmetry upon which the external symmetry of a crystal is based. Thus, even in distorted crystal that exhibit crystal faces, the symmetry can be determined by the angular relationships. This is easiest to see if we invoke a method of projection of crystallographic angles called stereographic projection.

Stereographic Projection

Stereographic projection is a method used in crystallography and structural geology to depict the angular relationships between crystal faces and geologic structures, respectively. Here we discuss the method used in crystallography, but it is similar to the method used in structural geology.

Imagine again that we have a crystal inside of a sphere. This time, however we will first look at a cross-section of the sphere as shown in the left-hand diagram below. We orient the crystal such that the pole to the (001) face (the c axis) is vertical and points to the North pole of the sphere. For the (011) face we draw the pole to the face to intersect the outside of the sphere. Then, we draw a line from the point on the sphere directly to the South Pole of the sphere. Where this line intersects the equatorial plane is where we plot the point. The stereographic projection then appears on the equatorial plane.

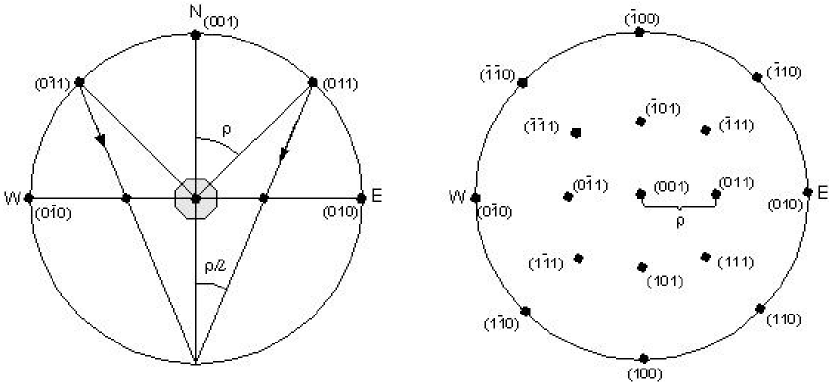


Fig. (63): The stereographic projection of a crystal .

In the right hand-diagram we see the stereographic projection for faces of an isometric crystal. Note how the ρ angle is measured as the distance from the center of the projection to the position where the crystal face plots. The φ angle is measured around the circumference of the circle, in a clockwise direction away from the b crystallographic axis or the plotting position of the (010) crystal face.

In order to make plotting of the stereographic projection easier, a device called a stereographic net or stereonet is used. Such a stereonet is shown in the diagram below. Although the North (N) and South (S) poles are shown on the stereonet, these do not correspond to the North and South Poles as defined in the projection above. However, when plotting directional data in structural geology, they do represent the North and South geographic directions.

As defined in our projection, the N and S poles would plot directly above and below the center of the stereonet.

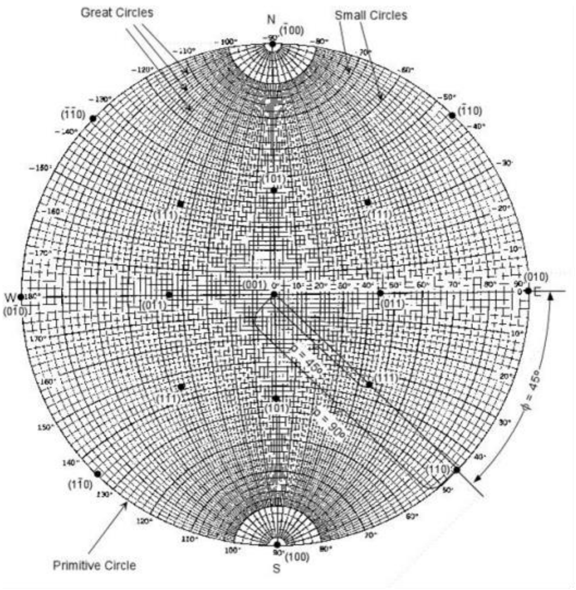


Fig. (64): The stereographic net or stereonet.

On the stereonet, we see several different components that we define here.

The Primitive Circle is the circle that surrounds the stereonet.

Great Circles are the curved lines that connect the points labeled N and S on the stereonet. The E-W and N-S axes, as well as the Primitive Circle are also great circles.

Angular relationships between points can only be measured on Great Circles.

Small Circles are the highly curved lines that curve upward and downward on the stereonet.

The upper faces of an isometric crystal are plotted in the stereonet above. These faces belong to forms {100}, {110}, and {111}. Note that the faces (111) and (110) both have a φ angle of 45o. The ρ angle for these faces is measured along a line from the center of the stereonet (where the (001) face plots) toward the edge. For the (111) face the ρ angle is 45o, and for the (110) face the ρ angle is 90^o.

In Lab, your lab instructor will show you how to construct a stereonet for plotting crystal faces. This will consist of a stereonet mounted on a piece of cardboard with a thumbtack through the center. You can then place a sheet of tracing paper on the stereonet and rotate it around the thumb tack. The following rules are then applied:

1. All crystal faces are plotted as poles (lines perpendicular to the crystal face. Thus, angles between crystal faces are really angles between poles to crystal faces.

2. The b crystallographic axis is taken as the starting point. Such an axis will be perpendicular to the (010) crystal face in any crystal system. The [010] axis (note zone symbol) or (010) crystal face will therefore plot at $\varphi = 0^o$ and $\rho = 90^o$.

3. Positive φ angles will be measured clockwise on the stereonet, and negative φ angles will be measured counter-clockwise on the stereonet.

4. Crystal faces that are on the top of the crystal ($\rho < 90^o$) will be plotted as open circles, and crystal faces on the bottom of the crystal ($\rho > 90^o$) will be plotted as "+" signs.

5. Place a sheet of tracing paper on the stereonet and trace the outermost great circle. Make a reference mark on the right side of the circle (East).

6. To plot a face, first measure the φ angle along the outermost great circle, and make a mark on your tracing paper. Next rotate the tracing paper so that the mark lies at the end of the E-W axis of the stereonet.

7. Measure the ρ angle out from the center of the stereonet along the E-W axis of the stereonet. Note that angles can only be measured along great circles. These include the primitive circle, and the E-W and N-S axis of the stereonet.

8. Any two faces on the same great circle are in the same zone. Zones can be shown as lines running through the great circle containing faces in that zone. The zone axis can be found by setting two faces in the zone on the same great circle, and counting 90o away from the intersection of the great circle along the E-W axis.

9. To plot symmetry axes on the stereonet, use the following conventions:

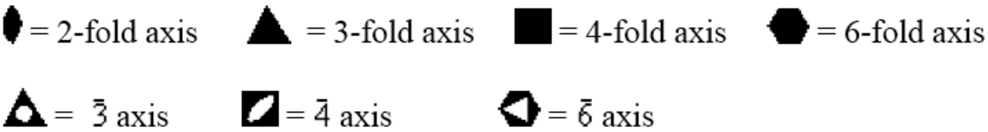


Fig. (65): The symmetry axes conventions used for plotting on the stereonet.

As an example all of the faces, both upper and lower, for a crystal in the class 4/m 2/m in the forms {100}(hexahedron - 6 faces), {110} (dodecahedron, 12 faces), and {111} (octahedron, 8 faces) in the stereogram to the right. Rotation axes are indicated by the symbols as discussed above. Mirror planes are shown as solid lines and curves, and the primitive circle represents a mirror plane.

Note how the symmetry of the crystal can easily be observed in the stereogram.

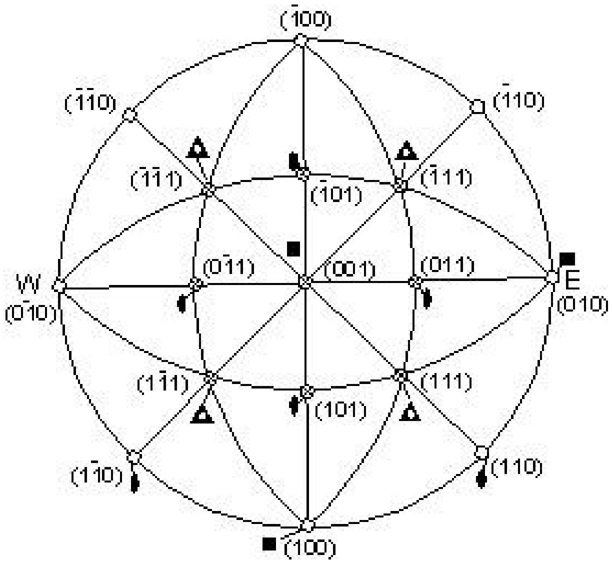


Fig. (66): The final stereogram of a crystal on the stereonet.

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https://en.wikipedia.org/wiki/Crystal_system; Includes symmetry operations, point groups, and space groups

Crystallography Learning Objectives

By the end of this courser the student should be able to do the following:

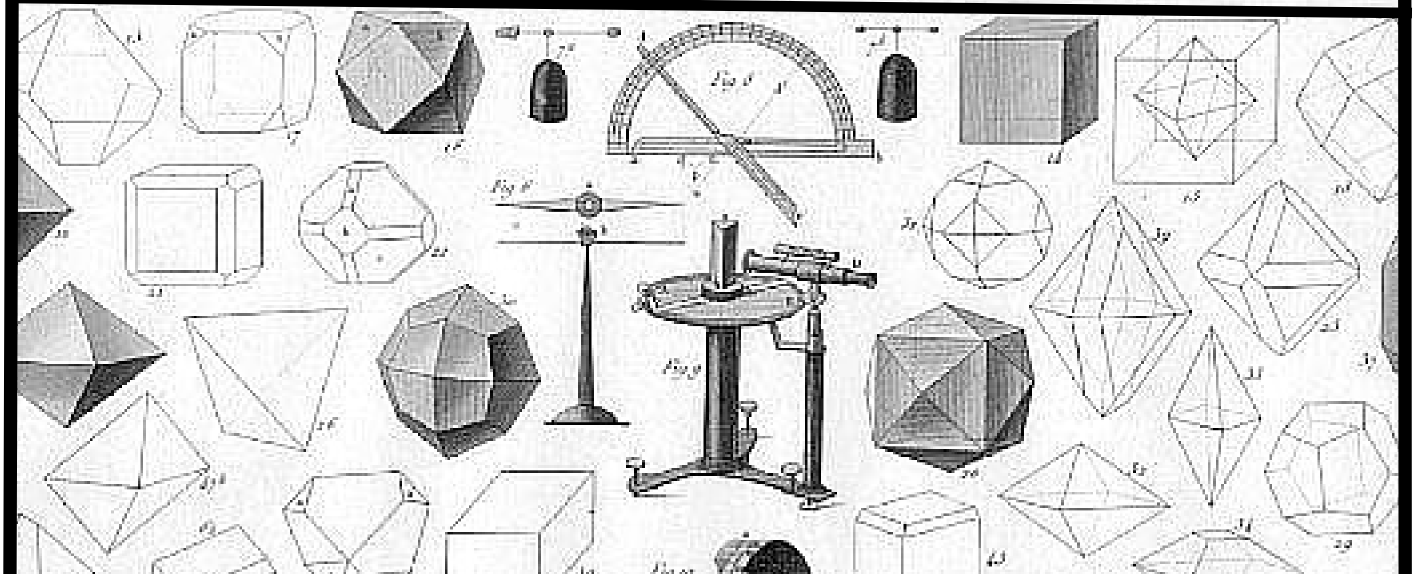
- Describe the operation of the following symmetry operators: rotation axes and inversion axes, of orders 1, 2, 3, 4 and 6; a mirror plane and a center, and be able to demonstrate their operation on a sketch stereogram.
- Name the minimum set of symmetry elements possessed by each of the seven crystal systems and be able to assign a crystal to the correct system, given its symmetry elements.
- Understand the notation of the 32 crystal classes (point groups) and be able to draw sketch stereograms illustrating the operation of a given point group of symmetry elements on a general pole (hkl).
- Understand the principles by which symmetry operators can be combined by reference to the crystal classes in the orthorhombic, monoclinic and triclinic systems – i.e. know why, for example, mmm, mm and 222 are the only three classes in the orthorhombic system.
- Understand the Miller and Miller-Bravais systems of indexing crystal faces and be able to describe how the orientation of a given face relates to the crystallographic axes and unit repeats.
- Plot an accurate stereogram of a crystal with orthogonal axes, given measured interfacial angles in a series of zones; identify the symmetry elements from the projection; assign crystallographic axes consistent with normal conventions; choose an appropriate face as {111}, and so index the other faces.
- Calculate axial ratios in tetragonal and orthorhombic crystals, given the angles between appropriate known faces.
- Define and/or explain the terms zone, zone axis, axial ratio, general form and special form.
- Define and be able to explain the concept of a lattice as distinct from a crystal’s structure. Define lattice point, lattice row, lattice plane, lattice space and unit cell.
- State and explain the Law of the Constancy of Interfacial Angles and the Law of Rational Intercepts by reference to the lattice concept.
- Understand in principle the relationship between axial ratios determined by a study of a crystal’s external form and the axial ratio derived from a study of a mineral’s internal structure.
- Describe, draw and name the seven primitive and seven non-primitive Bravais lattices to which all crystalline material belong, and explain, in principle why the number of such possible lattices is limited, by giving examples of lattices which are equivalent.
- Understand in principle the distinction between point symmetry elements (which operate through a point without moving it) and translational symmetry elements by which real crystal structures can be organized.

Crystallography

Practical Course

Faculty of Science
South Valley University

Prepared by/Ali Ismail Ali



2015

Course outline

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(4) Hexagonal system	13	6,7
(5) Trigonal system	17	8,9
(6) Cubic system	21	10,11
(7) Monoclinic system	25	12
(8) Triclinic system	29	13
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Crystallography

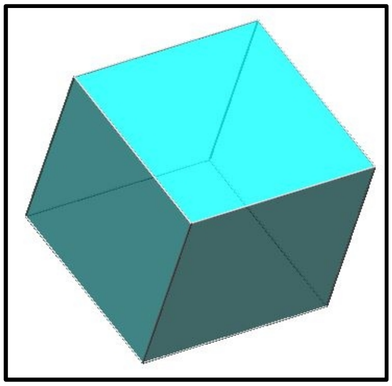
علم البلورات

تعريف علم البلورات :

هو احد علوم المعادن و الصخور في الجيولوجيا . علم البلورات يختص بدراسة البلورات من حيث شكلها الظاهري أو الخارجي وتركيبها والتعرف عليها وعلى الصخور والمعادن التي تحويها.

- **تعريف البلورة:**

جسم صلب متجانس له سلسلة ذرية متكررة ثلاثية الأبعاد، و ذو بنية داخلية منظمة، تحدها أسطح مستوية تكونت بفعل العوامل الطبيعية تحت ظروف مناسبة ويسمى كل سطح وجه بلوري.



- **أجزاء البلورة**:

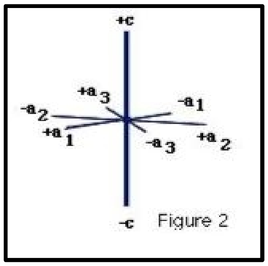
.1	الأوجه البلورية	crystal faces
.2	الأحرف	edges
.3	الزوايا بين الأوجه	interfacial angles
.4	الزوايا المجسمة	Solid angles

- **المتقاطع المحورى Axial cross**

وينتج عن تقاطع المحاور البلورية (يتكون من المحاور والزوايا بينها)

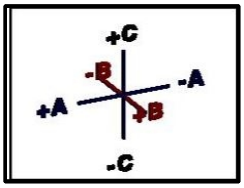
-1 المحاور البلورية Crystallographic axes

المحاور البلورية هي عبارة عن ثلاثة خطوط تصورية أو خيالية ، (أربعة في فصيلتي السداسي والثلاثي) والتي يمكن رسمها داخل البلورة بحيث تتقاطع في مركز البلورة ، وتعمل كخطوط ترجع إليها كلما أردنا وصف مواضع الأوجه البلورية (كل وجه لابد أن يقطع واحدا أو أكثر من هذه المحاور البلورية على مسافة معينة من المركز). يرمز لها (a,b,c) او (a1,a2,a3 ,c) في حالة فصيلتي السداسي و الثلاثي ونفرق أطوال هذه المحاور بواسطة استعمال الإشارات الموجبة (+) ، والسالبة(-)



2 - الزوايا المحورية زوايا ناتجه عن تقاطع هذه المحاور الثلاثة وهى :

- زاوية ألفا (α) بين b ، c
- وزاوية بيتا (β) بين a ، c
- ، وزاوية جاما (δ) بين a ، b.



- **توجيه المحاور البلورية**

المحور a من الأمام إلى الخلف والمحور b من اليمين الى اليسار والمحور c من اعلى الى اسفل

وعلى أساس أطوال المحاور البلورية، والزوايا بين هذه المحاور ، يمكننا لتمييز بين الفصائل البلورية السبعة.

- **تعليمات بشأن اختيار المحاور البلورية :**

الفصيلة	القاعدة
فصيلة المكعب	**المحاور الرباعية التماثل هي المحاور البلورية**
فصيلة السداسي	**المحور السداسي التماثل هو المحور c ، وأطول ثلاثة محاور ثنائية التماثل هي المحاور a1,a2,a3**
فصيلة الرباعي	**المحور الرباعي التماثل هو المحور c ، وأطول محورين ثنائي التماثل هما ، .b,c**
فصيلة الثلاثي	**المحور الثلاثي التماثل هو المحور c ، و الثلاث محاور ثنائية التماثل هي المحاور a1,a2,a3**
فصيلة المعيني القائم	**الثلاثة محاور الثنائية التماثل هي المحاور البلورية ، وفي العادة يختار c أطول من b ، وb أطول من a .**
فصيلة الميل الواحد	**المحور الثنائي التماثل هو المحور b ، يختار بعد ذلك المحور c موازيا لحروف أربعة أوجه متشابهة تماما والتي تعتبر مكونة للشكل المنشوري ، وبعد ذلك يختار المحور a موازيا للسطحين الذين يقطعان أوجه المنشور بزاوية تقرب من القائمة**
فصيلة الميول الثلاثة	**ابحث عن ثلاثة أزواج من السطوح المتوازية التي تتقاطع مع بعضها بزوايا تقرب من القائمة والتي تحد الفراغ كعلبة كبريت مشوهة ، وتختار المحاور البيلورية موازية لهذه الأسطح (كل محور موازي لمجموعتين من هذه المجموعات**

- **الفصائل البلورية :**

النظام البلوري في علم البلورات، عبارة عن نظام يسهم في تصنيف المعادن و البلورات حسب التناظر الهندسي لها في فضاء ثلاثي الأبعاد.
يوجد سبع فصائل بلورية تتبعها المعادن عند التبلور ، تسمي الفصائل أو الأنظمة البلورية كما هو موضح في الجدول :

الفصيلة Crystal Systems	المتقاطع المحوري		التماثل المميز
	المحاور البلورية	الزوايا المحورية	
فصيلة المكعب Cubic System	(a=b=c)	(α=β=δ=90)	أربعة محاور ثلاثية
فصيلة الرباعي Tetragonal System	(a=b‡c)	(α=β=δ=90)	محور واحد رباعي
فصيلة سداسي Hexagonal System	(a1=a2=a3‡c)	(α = β =90‡ δ =120)	محور سداسي
فصيلة ثلاثي) Trigonal System	(a1=a2=a3‡c)	(α =β =90 ‡δ =120)	محور واحد ثلاثى
فصيلة المعيني القائم Orthorhombic System	(a‡b‡c)	(α=β=δ=90)	ثلاثة محاور ثنائية
فصيلة أحادي الميل Monoclinic System	(a‡b‡c)	(α=δ=90,β‡90)	محور واحد ثنائي
فصيلة ثلاثي الميول Triclinic System	(a‡b‡c)	(α‡β‡δ‡90)	---------

اهم المعادن والفصائل التي تتبعها :

الفصيلة Crystal Systems	اهم المعادن التي تتبعها
فصيلة المكعب Cubic System	بيريت ، هاليت ، جالينا ، الالماس ، فلوريت
فصيلة الرباعي Tetragonal System	وولفرينيت ، روتيل ، زركون ، كالكوبيريت
فصيلة سداسي Hexagonal System	كوارتز ، بيريل ، اباتيت ، كوراندم (الياقوت والصفير)
فصيلة ثلاثي) Trigonal System	كالسيت ، دولوميت
فصيلة المعيني القائم Orthorhombic System	الكبريت ، باريت، الاولوفين ، التوباز
فصيلة أحادي الميل Monoclinic System	اورثوكليز ، ملاكيت ، ازوريت ، ميكا ، جبس ، تلك
فصيلة ثلاثي الميول Triclinic System	الكيانيت ، البلاجيوكليز

Crystal system : Orthorhombic المعينى القائم

Axial cross : المتقاطع المحورى

Crystallographic axes: المحاور البلورية a‡b‡c

Axial angles : الزوايا المحورية α=β=δ=90

Holosymmetric class النظام كامل التماثل:Rhombic bi pyramidal (منعكس) هرم معينى مزدوج

symbol : 2/m 2/m 2/m

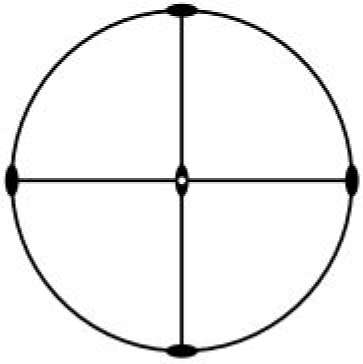
Elements of symmetry:

Axes of symmetry: ⬬3

Planes of symmetry : 3m

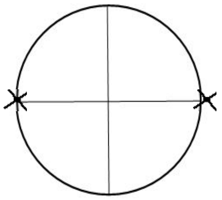
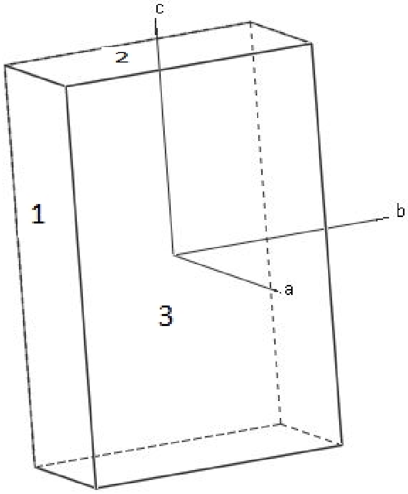
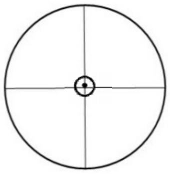
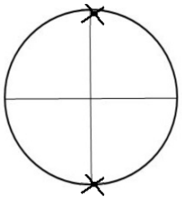
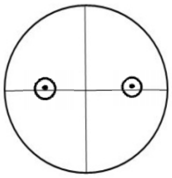
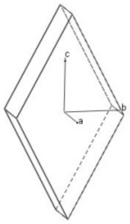
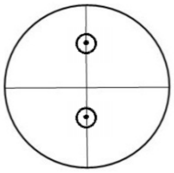
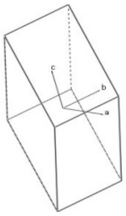
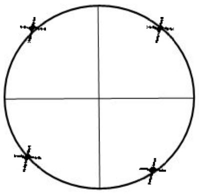
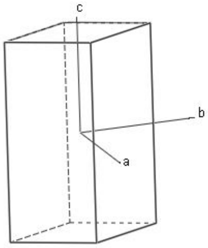
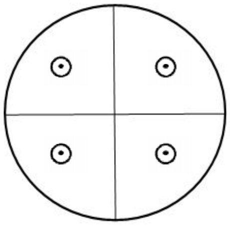
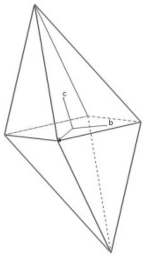
Center of symmetry: i

stereographic projection of elements of symmetry:



$\frac{2}{m}\frac{2}{m}\frac{2}{m}$

Crystal forms of holosymmetric class

Pinacoid المسطوح Number of faces (2) Form expression : open	**Side pinacoid** (b- pinacoid) مسطوح جانبى Indices : (010)	 1	
	Basal pinacoid (c- pinacoid) مسطوح قاعدى Indices : (001)	 2	
	Front piacoid (a-pinacoid) مسطوح امامى Indices : (100)	 3	
Dome : القبة Number of faces (4) Form expression : open	Side dome (a- dome) قبة جانبية Indices : (011)		
	Front dome (b- dome) قبة امامية Indices : (101)		
Orthorhombic prism : منشور معينى قائم Number of faces (4) Indices : (110) Form expression : open			
Rhombic bi pyramidal : هرم معينى قائم Number of faces (8) Indices : (111) Form expression : closed			

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal system : Tetragonal فصيلة الرباعي

Axial cross :

Crystallographic axes: a=b‡c

Axial angles : α=β=δ=90

Holosymmetric class: Di tetragonal- bi pyramidal الهرم المزدوج الرباعي الثنائي

symbol : 4/m 2/m 2/m

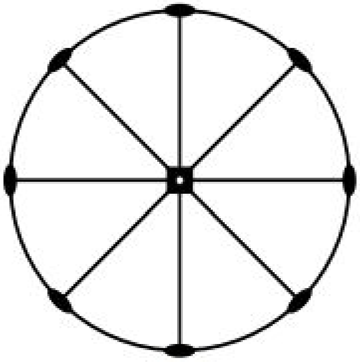
elements of symmetry:

⬬ ■
Axes of symmetry: 4 1

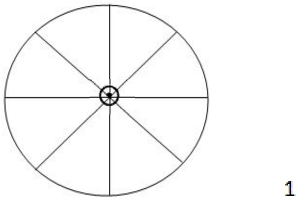
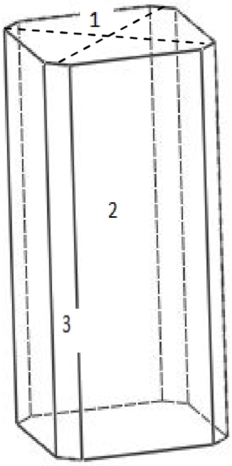
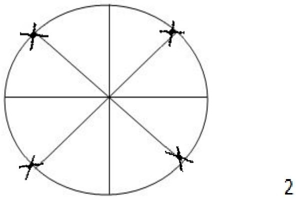
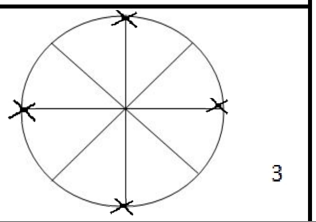
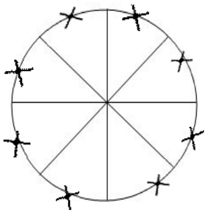
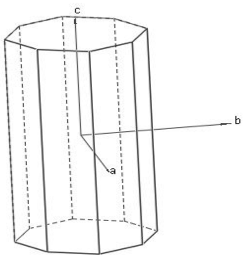
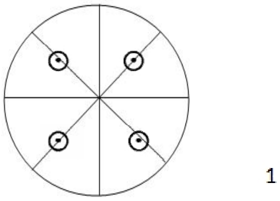
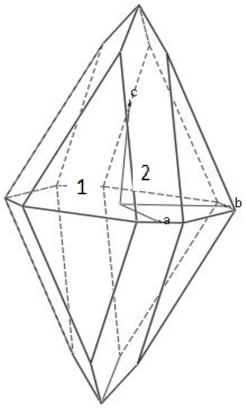
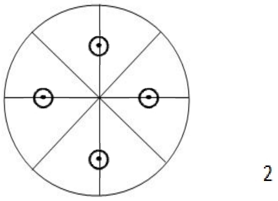
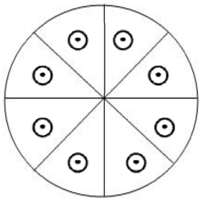
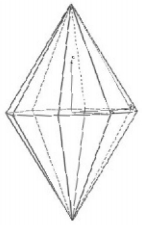
Planes of symmetry : 5m

Center of symmetry: i

Stereographic projection of elements of symmetry:



$\frac{4}{m}\frac{2}{m}\frac{2}{m}$

Crystal forms of holosymmetric class		
Basal pinacoid مسطوح قاعدى Number of faces : 2 Indices: (001) Form expression : open		
first order tetragonal Prism منشور رباعى رتبة اولى Number of faces : 4 Indices: (110) Form expression : open		
Second order tetragonal Prism منشور رباعى رتبة ثانية Number of faces : 4 Indices: (100) Form expression : open		
Di tetragonal prism منشور رباعي مزدوج Number of faces : 8 Indices: (210) Form expression : open		
First order Tetragonal bi-pyramidal هرم مزدوج رباعى رتبة اولى Number of faces : 8 Indices: (111) Form expression : closed		
second order Tetragonal bi-pyramidal هرم مزدوج رباعى رتبة ثانية Number of faces : 8 Indices: (101) Form expression : closed		
Di tetragonal bi-pyramidal هرم مزدوج رباعى ثنائى Number of faces :16 Indices: (112) Form expression : closed		

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal system : Hexagonal السداسي

Axial cross :

Crystallographic axes: **a1=a2=a3‡c**

axial angles : **α=β=90‡δ=120**

Holosymmetric class: Di hexagonal bi pyramidal هرم مزدوج سداسي ثنائي

Symbol : **6/m 2/m 2/m**

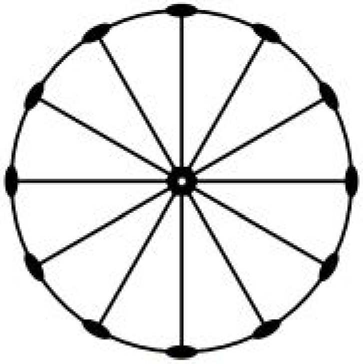
Elements of symmetry:

⬬ ⬢
Axes of symmetry: 6 , 1

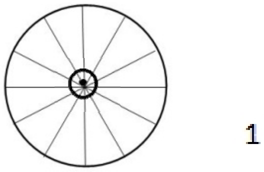
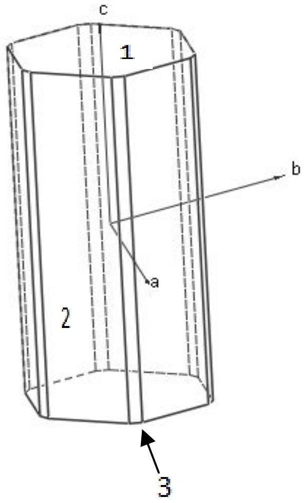
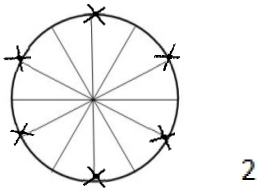
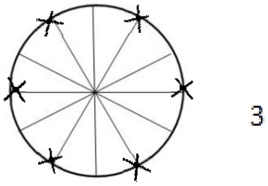
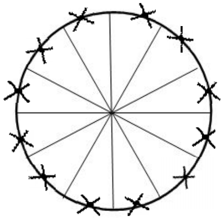
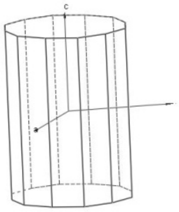
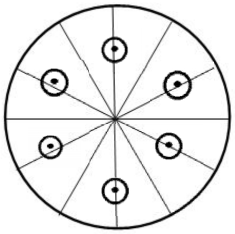
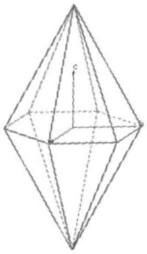
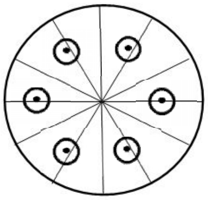
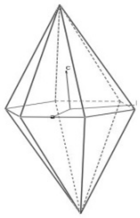
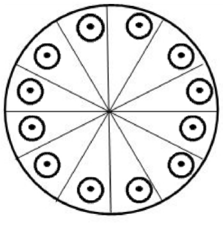
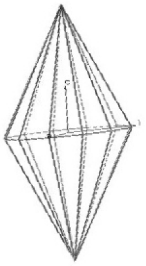
Planes of symmetry : 7m

Center of symmetry: i

Stereographic projection of elements of symmetry:



$\frac{6}{m}\frac{2}{m}\frac{2}{m}$

Crystal forms of holosymmetric class		
1.Basal pinacoid مسطح قاعدي Number of faces :2 Indices : (0001) Form expression :open		
2.First order hexagonal prism منشور سداسى رتبة اولى Number of faces :6 Indices : $(10\bar{1}0)$ Form expression :open		
3. Second order hexagonal prism منشور سداسي رتبة ثانية Number of faces :6 Indices : $(11\bar{2}0)$ Form expression :open		
4. Di hexagonal prism منشور سداسي مزدوج Number of faces :12 Indices : $(21\bar{3}0)$ Form expression :open		
5. First order hexagonal bi- pyramid هرم سداسي مزدوج رتبة اولى Number of faces :12 Indices : $(10\bar{1}1)$ Form expression :closed		
6. Second order hexagonal bi-pyramid هرم سداسي مزدوج رتبة ثانية Number of faces :12 Indices : $(11\bar{2}2)$ Form expression :closed		
7. Di hexagonal bi-pyramid هرم مزدوج سداسي ثنائي Number of faces :24 Indices : $(21\bar{3}1)$ Form expression :closed		

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal system : Trigonal الثلاثى

Axial cross :

Crystallographic axes: a1=a2=a3‡c

Axial angles : α=β=90‡δ=120

Holosymmetric class: **Ditrigonal Scalenohedron** سكالين (ذوالاوجه المثلثة غير متساوية الاضلاع) ثلاثي ثنائى

symbol : $3\ \bar{2}/m$

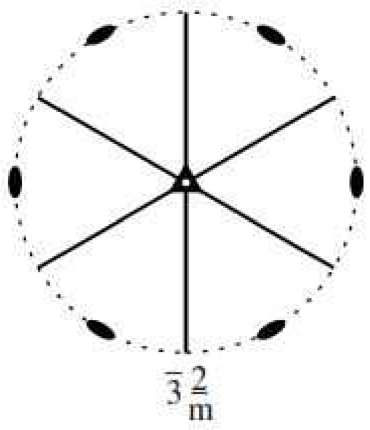
Elements of symmetry:

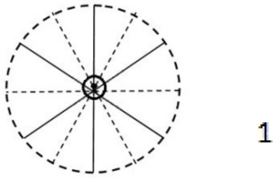
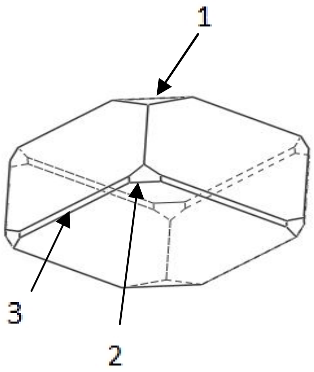
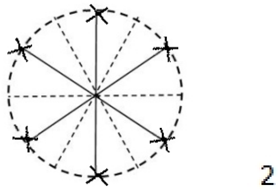
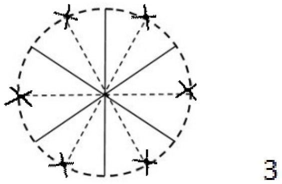
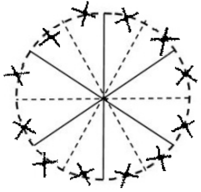
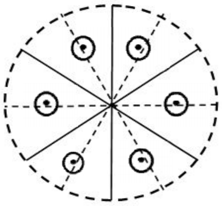
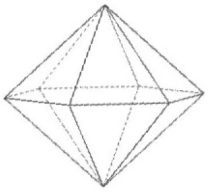
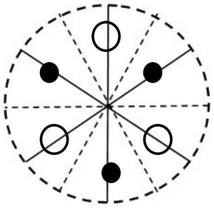
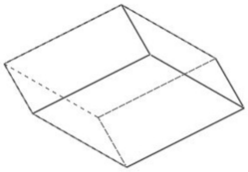
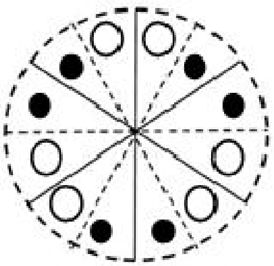
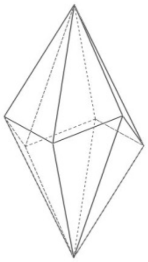
Axes of symmetry: 3 ⬬ 1 △

Planes of symmetry : 3m

Center of symmetry: i

Stereographic projection of elements of symmetry:



Crystal forms of holosymmetric class		
1.Basal pinacoid مسطح قاعدي Number of faces :2 Indices : (0001) Form expression :open		
2.First order hexagonal prism منشور سداسى رتبة اولى Number of faces :6 Indices : $(10\bar{1}0)$ Form expression :open		
3. Second order hexagonal prism منشور سداسي رتبة ثانية Number of faces :6 Indices : $(11\bar{2}0)$ Form expression :open		
4. Di hexagonal prism منشور سداسي مزدوج Number of faces :12 Indices : $(21\bar{3}0)$ Form expression :open		
6. Second order hexagonal bi pyramid هرم سداسي مزدوج رتبة ثانية Number of faces :12 Indices : $(11\bar{2}2)$ Form expression :closed		
Rhombohedron: معينى الاوجه Number of faces :6 Indices : $(10\bar{1}1)$ Form expression :closed		
Ditrigonal Scalenohedron **سكالين (ذوالاوجه المثلثة غير متساوية الاضلاع) ثلاثي ثنائى** Number of faces :12 Indices : $(21\bar{3}1)$ Form expression :closed		

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal system : cubic المكعب

Axial cross :

Crystallographic axes: **a=b=c**

Axial angles : **α=β=δ=90**

Holosymmetric class: Hexoctahedron ست ثمانية أوجه

Symbol : **4/m 3 $\bar{2}$/m**

Elements of symmetry:

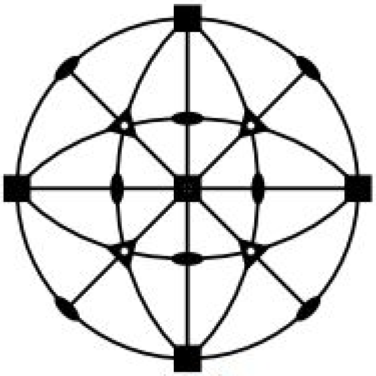
⬬ △ ■

Axes of symmetry: 6 4 3

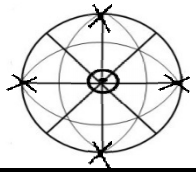
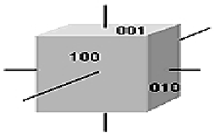
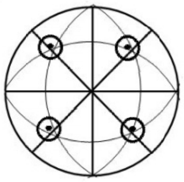
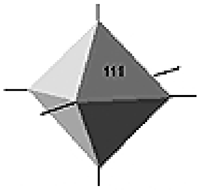
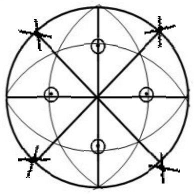
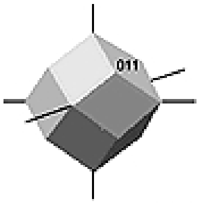
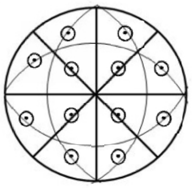
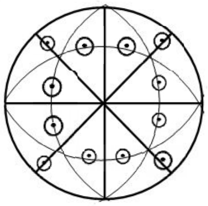
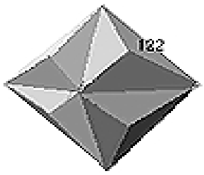
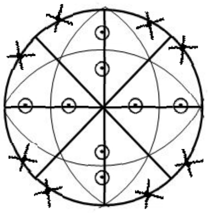
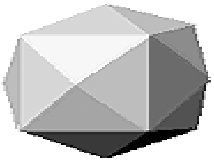
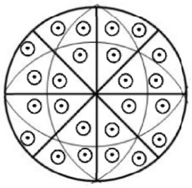
Planes of symmetry : 9m

Center of symmetry: i

stereographic projection of element of symmetry:



$\frac{4}{m}\bar{3}\frac{2}{m}$

Crystal forms of holosymmetric class		
Cube المكعب Number of faces : 6 Indices: (100) Form expression : closed		 3.2 Cube
Octahedron ذو الثمانية أوجه Number of faces : 8 Indices: (111) Form expression : closed		 3.3 Octahedron
Rhombic Dodecahedron **ذو الاثنى عشر وجها معينا** Number of faces : 12 Indices: (110) Form expression : closed		 3.4 Dodecahedron
Trapezohedron **ترابيز الاربعة وعشرون وجها** Number of faces : 24 Indices: (211)or **(hll)** Form expression : closed		
Trisoctahedron **ثلاث الثمانية اوجه** Number of faces : 24 Indices: (212) or **(hhl)** Form expression : closed		 3.9 Trisoctahedron
Tetra hexahedron **اربعة الست اوجه** Number of faces : 24 Indices: (210) or **(hk0)** Form expression : closed		 3.5 Tetrahexahedron
Hexoctahedron **ست الثمانية اوجه** Number of faces : 48 Indices: (321) or (hkl) Form expression : closed		 3.11 Hexoctahedron

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal system : Monoclinic أحادى الميل

Axial cross :

Crystallographic axes: a‡b‡c

Axial angles : α= δ=90‡ β‡90

Holosymmetric class: (hemi bi pyramid (نصف الهرم المزدوج

Symbol : 2/m

Elements of symmetry:

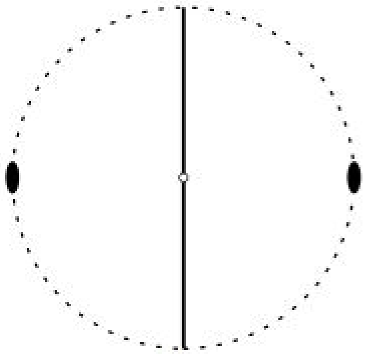
⬬

Axes of symmetry: 1

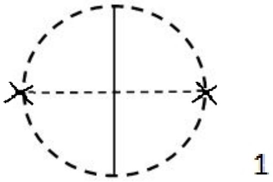
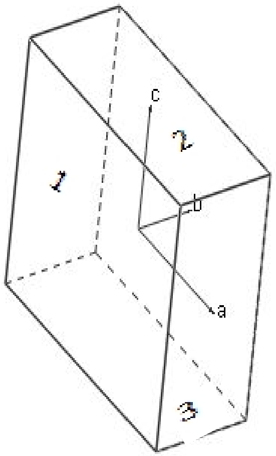
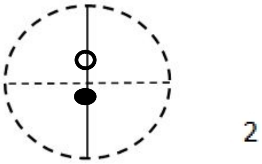
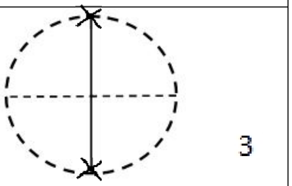
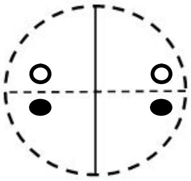
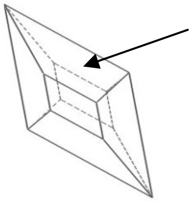
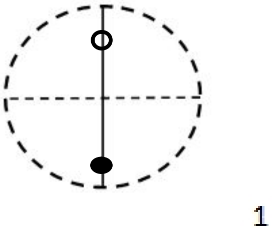
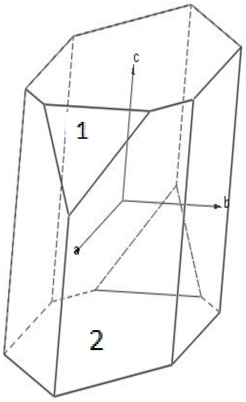
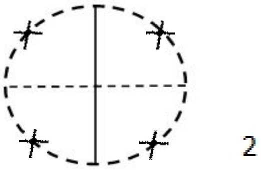
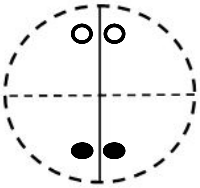
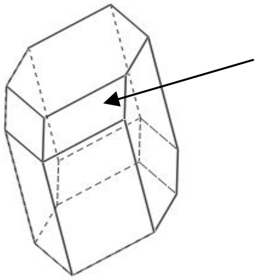
Planes of symmetry : 1m

Center of symmetry : i

stereographic projection of elements of symmetry :



2/m

Crystal forms of holosymmetric class			
Pinacoid المسطوح Number of faces (2) Form expression : open	**Side pinacoid** مسطوح جانبى Indices : (010)		
	Basal pinacoid مسطوح قاعدى Indices : (001)		
	Front pinacoid مسطوح امامى Indices : (100)		
Dome -a القبة Number of faces (4) Indices : (021) Form expression : open			
Hemi dome : نصف القبة Number of faces (2) Form expression : open Indices : (101)			
Monoclinic prism : منشور احادى الميل Number of faces (4) Indices : (110) Form expression : open			
Hemi bi pyramid : نصف الهرم Number of faces (4) Indices : (111) Form expression : open			

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal number :
Crystal system:
Number of crystal form :

Crystal form	Number of face	Indices

Crystal system : Triclinic ثلاثي الميول

Axial cross :

Crystallographic axes: a‡b‡c

Axial angles : α‡ β ‡ δ ‡90

Holosymmetric class: Pinacoidal نظام المسطحات

Symbol : $\bar{1}$

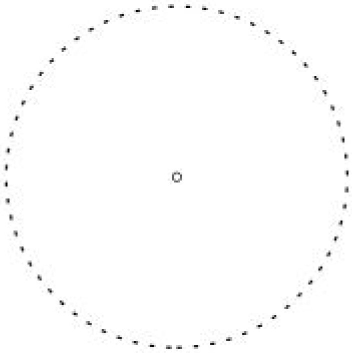
Elements of symmetry:

Axes of symmetry: none

Planes of symmetry : none

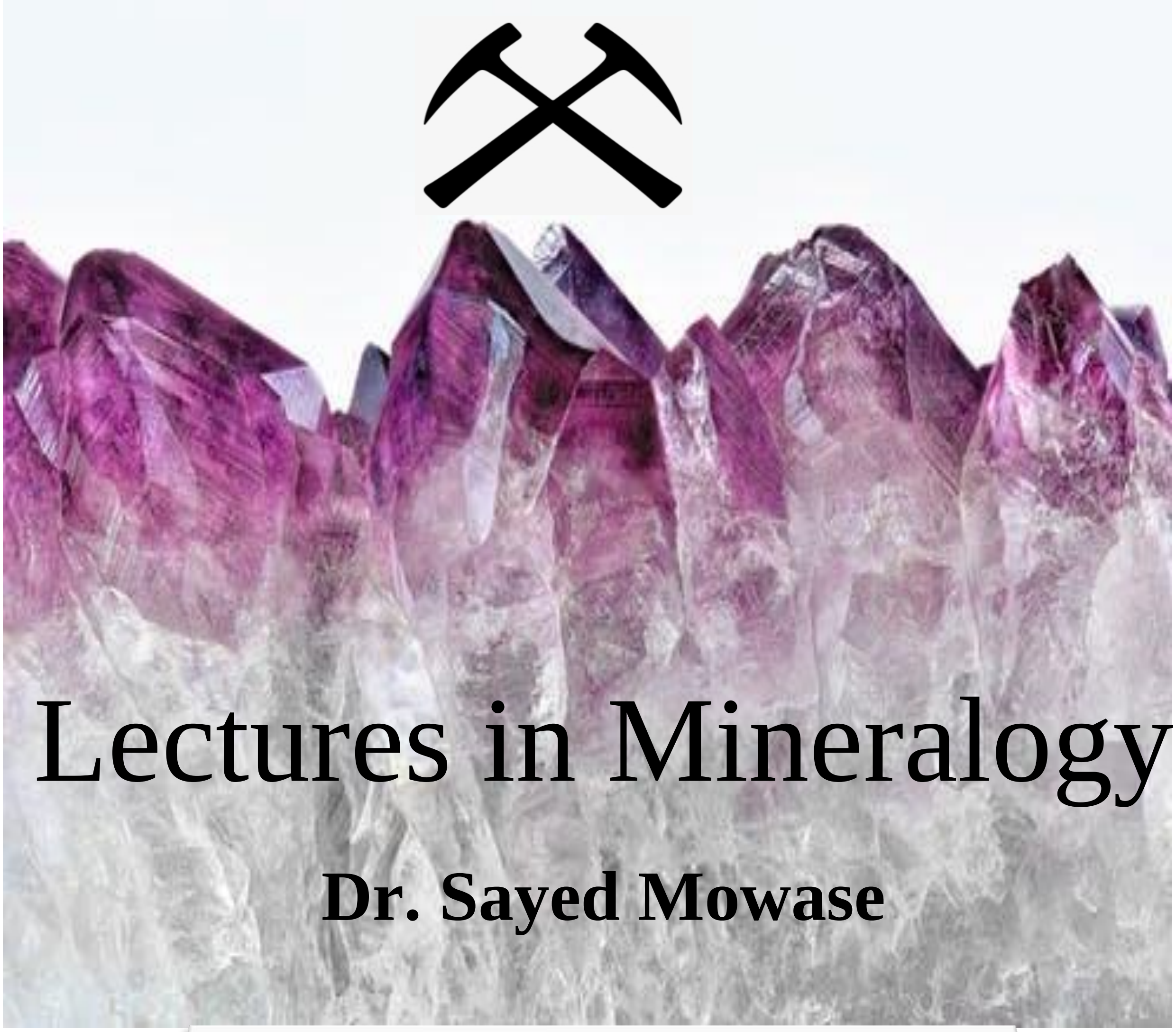
Center of symmetry: i

stereographic projection of elements of symmetry:



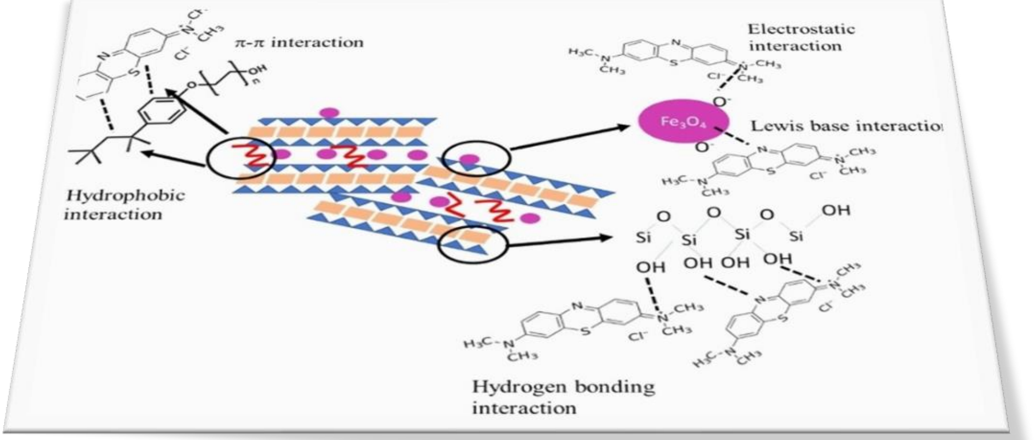
$\bar{1} = i$

More Practice, More Perfect



Lectures in Mineralogy

Dr. Sayed Mowase



<u>Geology</u>

Preface

There is a great relationship between geosciences and chemistry, which is reflected by the chemical composition of the rock-forming units, *minerals*. The nature of chemical bonding between the chemical constituents of a given mineral controls its physical and chemical properties such as cleavage, electrical conductivity, and the reaction with different acids and base. Moreover, some minerals are used as catalysts for different types of chemical reactions (e.g. kaolinite, quartz, smectite….etc).

The current course will give you a chance to take exciting trips every lecture through the principles of mineralogy: 1-*mineral definition; 2-Mineral-forming processes; 3-Physical and chemical properties of minerals; 4-Mineral classification*. Also, you will be kindly subjected to some aspects related to the mineral applications in chemical reactions and the industrial applications of some mineral types. Last but not least, you must ask more questions for yourself and your lecturer in order to learn more and more about mineralogy and to widen your knowledge and grow your thinking skills gradually.

My best regards,

Dr. Mahmoud Sabry Abdel-Hakeem

Contents

Part one: Mineralogy

Lecture#1: Mineral Definition and Crystallinity

1. Mineral Definition

Minerals are regarded as the main components of the different rock types. The term mineral refers to an inorganic naturally occurring solid material, which has a specific "not fixed" chemical composition and unique crystal structure (e.g. quartz, hematite, and calcite). The chemical makeup of most minerals is not fixed as a pure substance. Siderite, for example, does not always occur as pure iron carbonate($FeCO_3$); magnesium (Mg), manganese (Mn), and, to a limited extent, calcium (Ca) may sometimes substitute for the iron. So, the chemical formula of siderite can be expressed as (Fe, Mn, Mg, Ca) CO_3. This phenomenon is termed ionic substitution or solid solution, which results from the replacement of ion or ionic group by another in a particular crystal structure. **Three factors affect the substitution degree:**

1. The size of ions is one of the most important factors influencing the substitution degree. Ions of two different elements can freely replace one another if their ionic radii differ by approximately 15% or less. Limited substitution can occur if the radii differ by 15-30%, and a difference of more than 30% makes substitution unlikely.
2. The temperature at which crystals grow also plays a significant role in determining the extent of ionic substitution. The higher the temperature, the more extensive is the thermal disorder in the crystal structure and the less exacting are the spatial requirements. As a result, ionic substitution that could not have occurred in crystals grown at low temperatures may be present in those grown at higher ones. The high-temperature form of $KAlSi_3O_8$ (sanidine), for example, can accommodate more sodium (Na) in place of potassium (K) than can microcline, its low-temperature counterpart.
3. An additional factor affecting ionic substitution is the maintenance of a balance between the positive and negative charges in the structure. Replacement of a

monovalent ion (e.g., Na+, a sodium cation) by a divalent ion (e.g., Ca2+, a calcium cation) requires further substitutions to keep the structure electrically neutral.

$NaAlSi_3O_8$ ------------ $CaAl_2Si_2O_8$
Albite mineral----Anorthite mineral
Na^+& Si^{4+} -----------Ca^{2+}& Al^{3+}

<u>Note that</u> not all the solid naturally occurring materials can be considered as minerals, if they exhibit no ordered internal atomic arrangement. These materials are called amorphous (e.g. glass). Sometimes, two minerals have the same chemical composition, but they are different in the internal crystal structure. Graphite and diamond, for example, consist of carbon "C", however, graphite exhibit hexagonal crystals and diamond appears in the cubic form. *<u>This is called polymorphism</u>*.

- Graphite- hexagonal crystals, very soft (marks paper), density 2.3 g/cm^3.
- Diamond- cubic crystals, hardest known mineral, density 3.51 g/cm^3.

Diamond occurs in nature in rocks that were formed at extremely high pressure. To form diamonds in nature therefore requires a pressure of > 30 kb, which is equivalent to a depth of about 100 km below the Earth surface. To convert graphite to diamond in lab requires a pressure increasing to 100 kb at about 2500 ^oC (Figure 1).

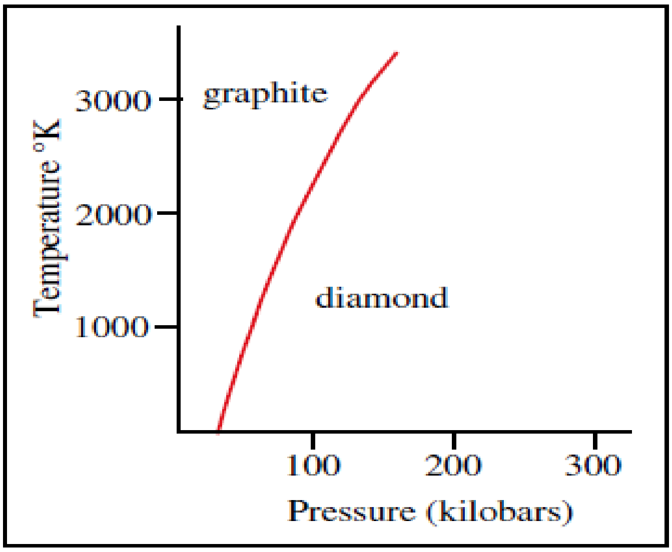


Figure 1: Pressure-Temperature phase diagram for carbon.

Depending on the ability of metal extraction, minerals can be grouped into:

- **Rock-forming minerals:**

The main compositional units of the different rock types: quartz, orthoclase, plagioclase, mica, calcite, olivine, siliminite……etc. These mineral types have several industrial applications, but cannot be exploited for metal extraction?????

- **Ore minerals:**

This category includes mineral substances contain high contents of valuable metal/s, making it suitable for the metallurgical processes (e.g. hematite, gold, pyrolusite, ilmenite…etc).

2. Mineral Crystallinity

The crystallization is a process in which one or more substances are transformed from liquid/or gas state into solid state depending on the ambient temperature and pressure conditions. As a result, the fast random movement of atoms gradually becomes slow down, and hence the atoms are closed and hold to each other by chemical bonds. The final 3-D arrangement of atoms is called *Crystal (solid materials characterized by highly ordered internal atomic structure)* and reflected outward in the form of *crystal faces*. *Unit cell* is the smallest unit of crystal volume, and by repeating its pattern in all directions, the entire crystal lattice can be constructed. For example, halite mineral is composed of Na and Cl atoms holding together by chemical bonds, with a three-dimensional order in the cubic form (Figure 2).

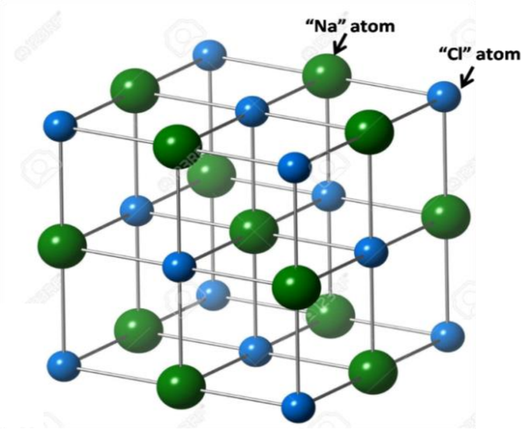


Figure 1: 3-Dimentional cubic arrangement of Na and Cl atoms of halite mineral.

Note: crystals differ from minerals due to their possible formation from both synthetic and natural processes (e.g. sugar cubes).

Minerals are crystallized in one or more crystal classes. There are seven crystal classes depending on the crystal elements and symmetry.

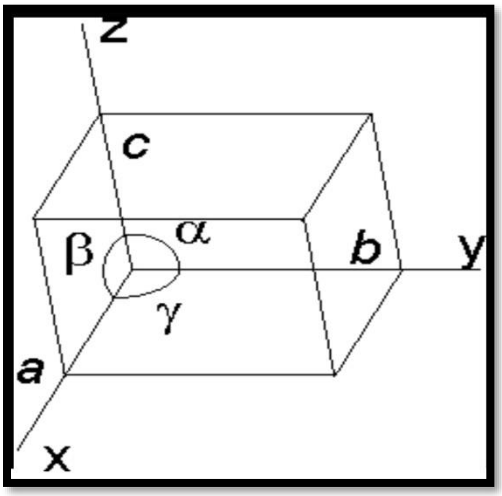
Crystal elements include:

- **Crystal axes:**

Crystal axes are imaginary lines passing through a crystal in important symmetry directions and intersecting in the crystal center. They are usually three in number "a"- "b"- "c" and sometimes four axes as "a_1"- "a_2"- "a_3" – "c".

- **Axial angles:**

The angles between the crystal axes are designed as:

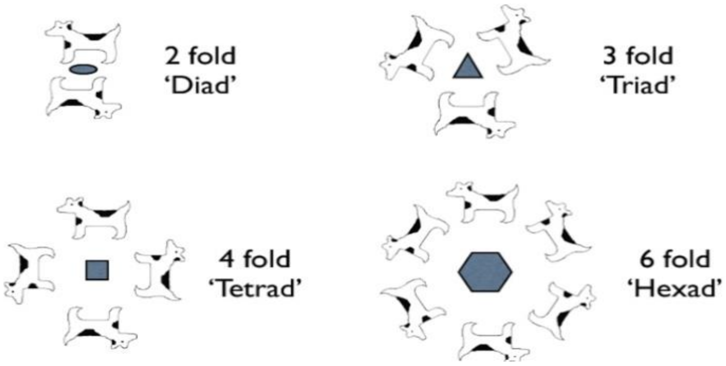


- **α** lies between b&c.
- **β** lies between a & c.
- **ɣ** lies between a & b.

Crystal Symmetry includes:

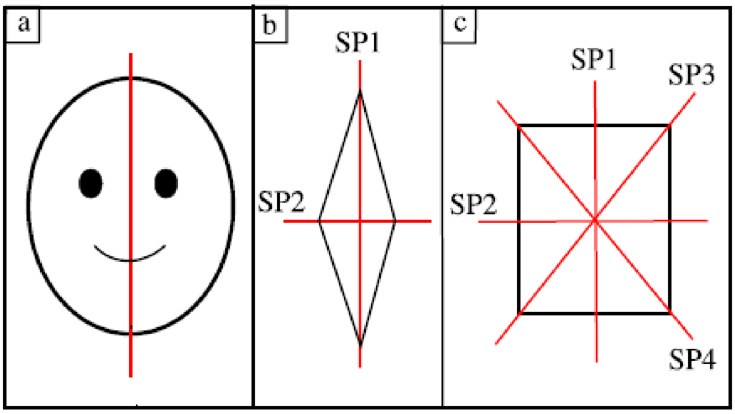
- **Symmetry axes:**

They are imaginary rotation axes by which one crystal face is repeated at 60°, 90°, 120° and 180° through 360° rotation. They are expressed as **two-fold, three-fold, four-fold, and six-fold.**



- **Symmetry planes:**

They are imaginary planes can split the crystal into two halves which are mirror of each other.

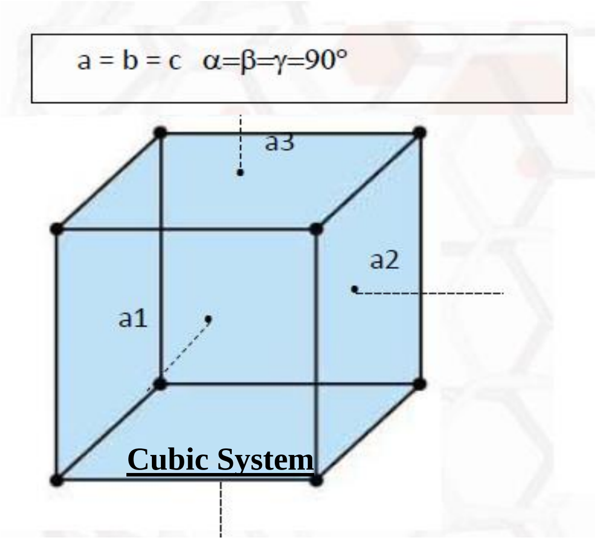


- **Symmetry center:**

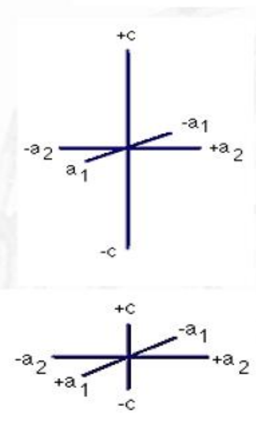
A center of symmetry exists in a crystal if an imaginary line can be extended from any point on its surface through its center and a similar point is present along the line equidistant from the center.

Depending on the crystal axes, axial angles, and symmetry elements, minerals can be found in one or more of **seven crystal systems:**

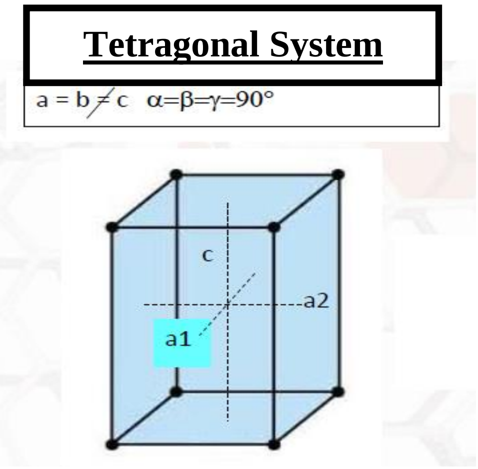
Crystal system	mineral examples
cubic	garnet, pyrite, halite (rock salt), magnetite
tetragonal	zircon
hexagonal	beryl
trigonal	calcite
orthorhombic	olivine, topaz
monoclinic	gypsum, orthoclase (K-feldspar)
triclinic	plagioclase (Ca-, Na-feldspar)



Cubic System

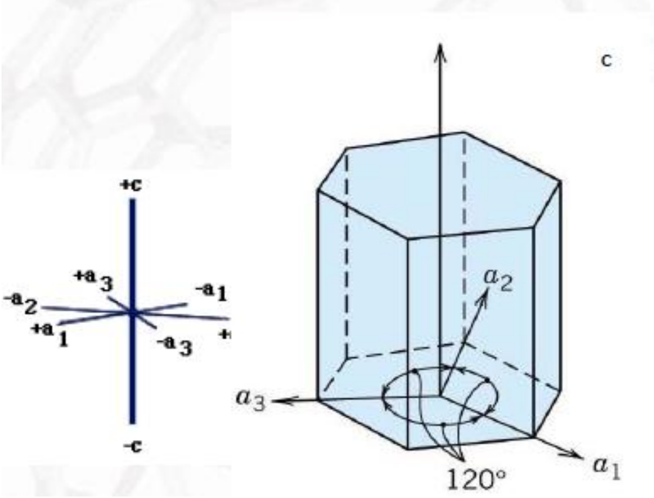


Tetragonal System



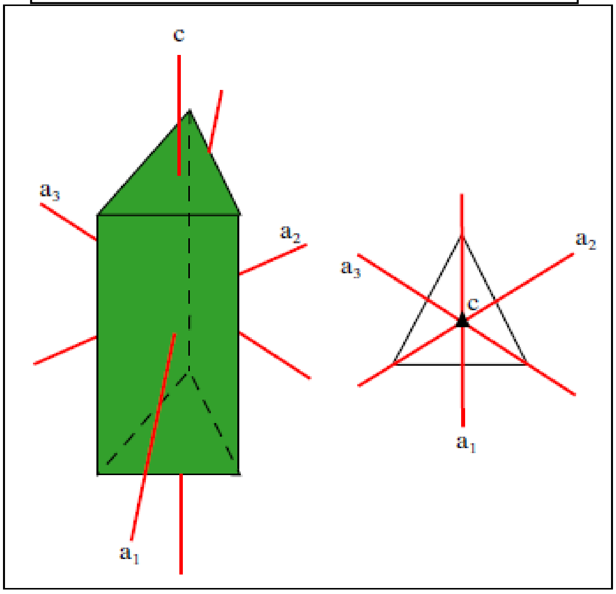
Hexagonal System

$a1=a2=a3 \neq c, \alpha=\beta=90^{o}, \gamma=120^{o}$



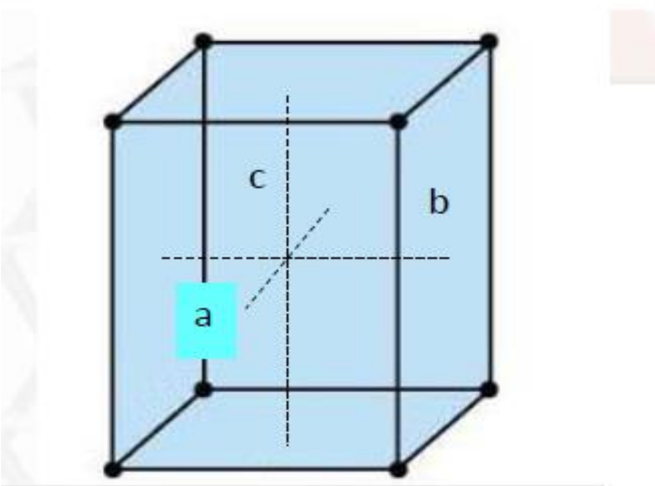
Trigonal System

$a1=a2=a3 \neq c, \alpha=\beta=90^{o}, \gamma=120^{o}$



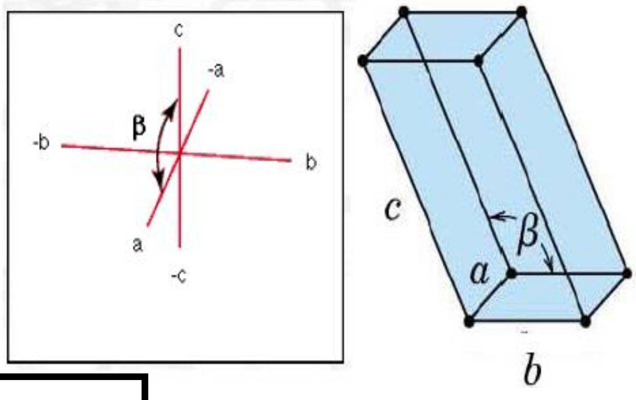
Orthorhombic System

$a \neq b \neq c \quad \alpha=\beta=\gamma=90^\circ$



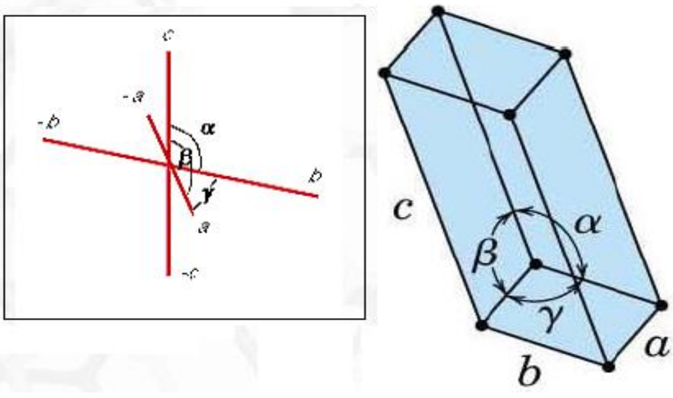
Monoclinic System

$a \neq b \neq c \quad \alpha=\gamma=90^\circ \neq \beta$



Triclinic System

$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$



Lecture#2: Chemical Bonding

3. Chemical Bonding

Chemical bonds are responsible for binding together the atoms, ions, and ionic groups that constitute crystalline solids. The physical and chemical properties of minerals are attributable for the most part to the types and strengths of these binding forces; hardness, cleavage, fusibility, electrical and thermal conductivity, and the coefficient of thermal expansion are examples of such properties. On the whole, the hardness and melting point of a crystal increase proportionally with the strength of the bond, while its coefficient of thermal expansion decreases. The extremely strong forces that link the carbon atoms of diamond, for instance, are responsible for its distinct hardness. Periclase (MgO) and halite (NaCl) have similar structures; however, periclase has a melting point of 2,800C (5,072 °F) whereas halite melts at 801 C (1,474 °F). This discrepancy reflects the difference in the bond strength of the two minerals: since the atoms of periclase are joined by a stronger electrical force, a greater amount of heat is needed to separate them.

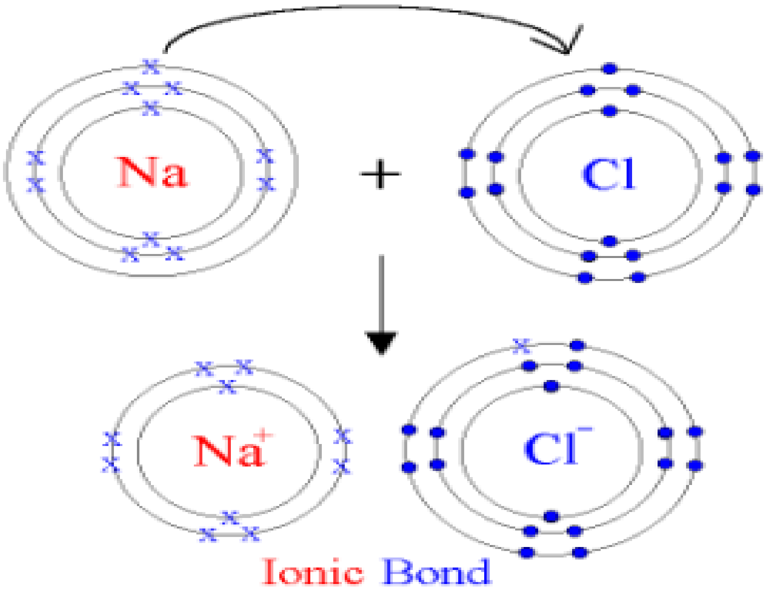
Chemical bonds are classified into five types

- 1-Ionic Bonds
- 2-Covalent Bonds
- 3-van der Waals Bonds
- 4-Metallic Bonds
- 5-Hydrogen Bonds

3.1. Ionic Bonds:

Atoms have a tendency to gain or lose electrons so that their outer orbitals become stable; this is normally accomplished by these orbitals being filled with the maximum allowed number of valence electrons. Metallic sodium, for example, has one valence electron in its outer orbital; it becomes ionized by readily losing this electron and exists as the cation Na+. Conversely, chlorine gains an electron to complete its outer orbital, thereby forming the anion Cl-. In the mineral halite, NaCl (common, or rock, salt), the chemical bonding that holds the Na+ and Cl- ions together is the attraction between the two opposite charges. This bonding mechanism is referred to as ionic bonding.

Note: Ionically bonded crystals typically display moderate hardness and specific gravity, rather high melting points, and poor thermal and electrical conductivity.



Illustrate, with drawing the electron-bearing orbitals, the ionic bond in minerals:

Sylvite $CaCl_2$,

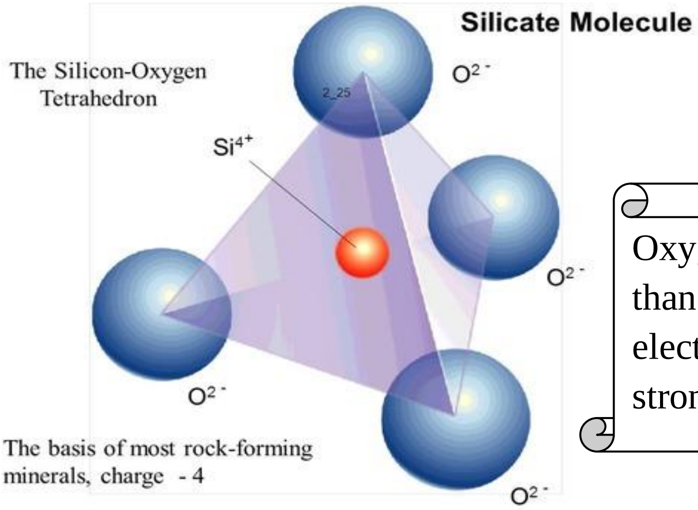
Galena PbS, and

Pyrite FeS_2

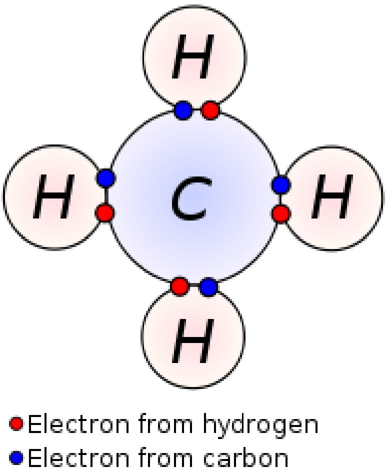
3.2. Covalent Bonds:

A covalent bond is formed by equal sharing of electrons from both the participating atoms. The pair of electrons participating in this type of bonding is called shared pair or bonding pair. The covalent bonds are also termed as molecular bonds. The electron-sharing, or covalent, bond is the strongest of all chemical bond types. **Minerals bonded in the manner display general insolubility, great stability, and a high melting point.**

Carbon, in the polymorphic form of diamond, is a good example of this type of covalent bonding. There are four valence electrons in a carbon atom, so that each atombonds with four others in a stable tetrahedral configuration.Diamond does not conduct electricity, because all thevalence electrons of its constituent atoms are shared to form bonds and therefore ***are not mobile***

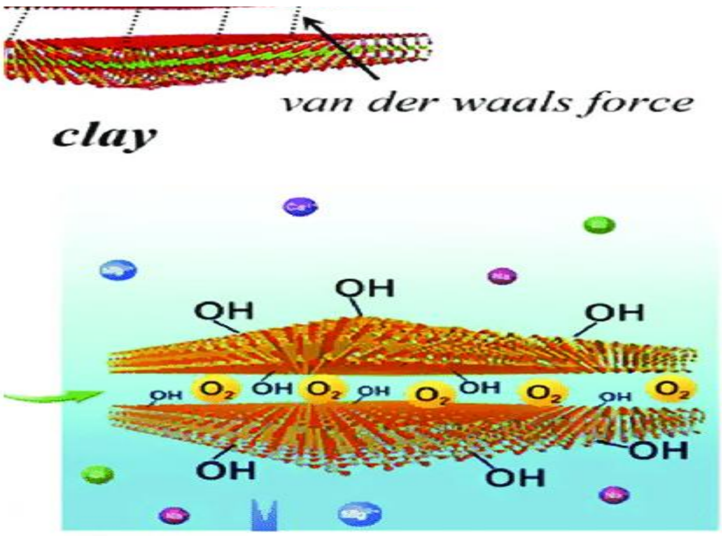


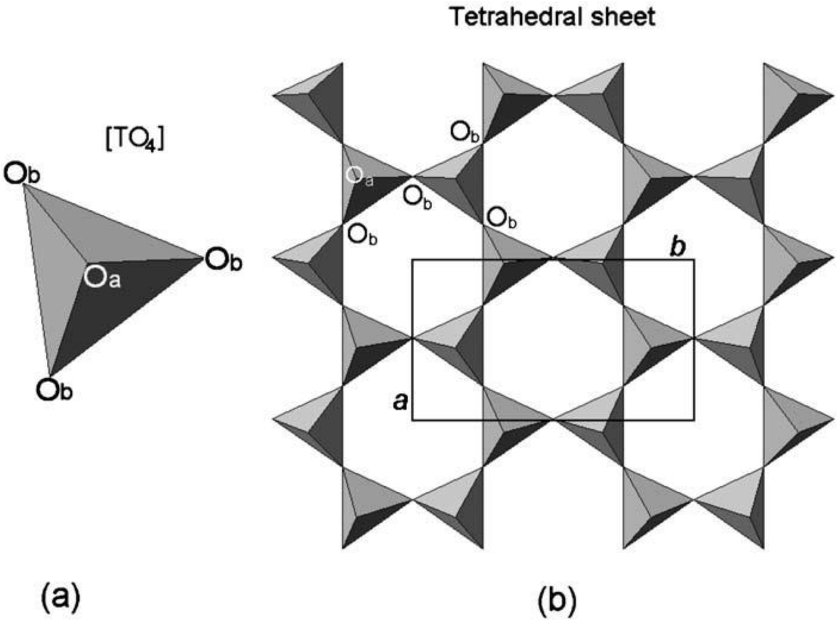
Oxygen has high erelectronegativity than Si, so oxygen attracts Si electrons for more time, making strong covalent bonding.



3.3. van der Waals Bonds:

Neutral molecules may be held together by a weak electric force known as the van der Waals bond. It results from the distortion of a molecule so that a small positive charge develops on one end and a corresponding negative charge develops on the other. A similar effect is induced in neighbouring molecules, and this dipole effect propagates throughout the entire structure. van der Waals forces are responsible for the attraction between **the tetrahedral and octahedral sheet of clay minerals**, resulting in swelling and fissility of the clay structure.

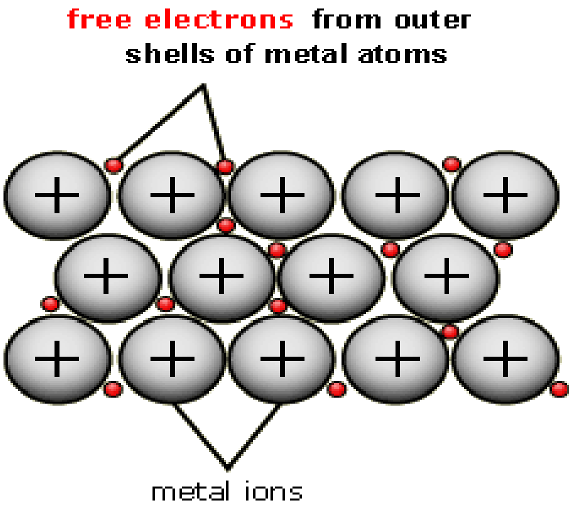


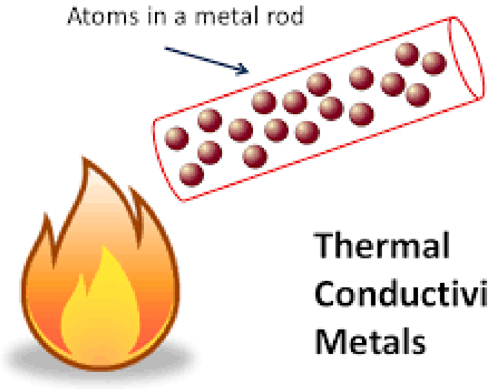


(a) Tetrahedron [TO4]; (b) tetrahedral sheet.Oa and Ob refer to apical and basal oxygen atoms, respectively

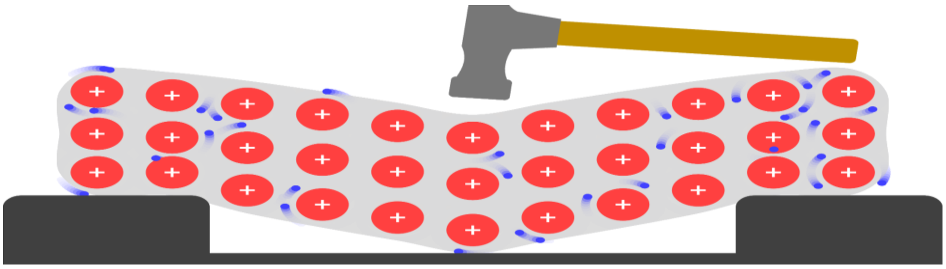
3.4. Metallic Bonds:

A metallic bond is a type of chemical bond formed between positively charged atoms in which the free electrons are shared among a lattice of cations.In contrast, covalent and ionic bonds form between two discrete atoms. Metallic bonding is the main type of chemical bond that forms between metal atoms.The electrons are not bound to any particular cation and are thus free to move throughout the structure.Electron mobility is responsible for the ability of metals to conduct heat and electricity.The native metals are the only minerals to exhibit pure metallic bonding.





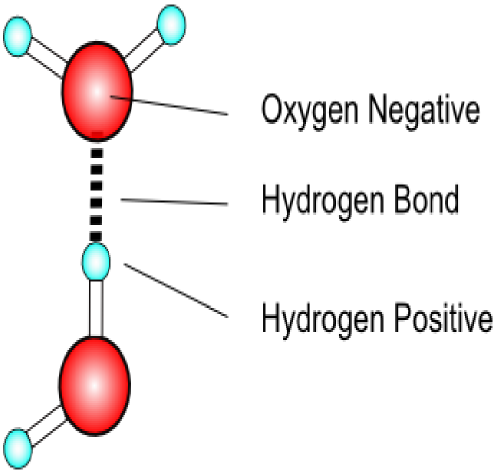
Thermal Conductivity of Metals



Plasticity of Metals

3.5. Hydrogen Bonds:

This takes place when a hydrogen atom, bonded to an electronegative atom such as oxygen, fluorine, or nitrogen, is also attracted to the negative end of a neighbouring molecule. A strong dipole-dipole interaction is produced, forming a bond between the two molecules. Hydrogen bonding is common in hydroxides and in many of the layer silicates (e.g., micas and clay minerals). Hydrogen bond contributes to the attraction between the water molecules and oxygen atoms on the clay surface, resulting in weak bonding between clay layers due to more adsorption of water molecules.



Some questions to be answered:

- Halite has melting point lower than kaolinite, why?
- Copper has higher heat conductivity than orthoclase, why?
- The individual sheets of clay minerals are stronger than the connected sheets, why?
- Diamond is water-insoluble comparing with sylvite, why?
- Structures of clay minerals have a negative charge, why?

Lecture#3: Properties of Minerals

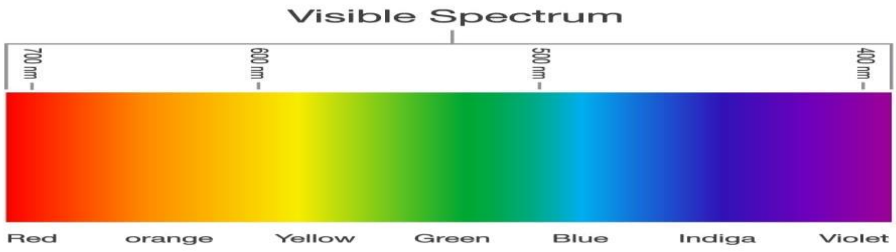
4. Properties of Minerals:

We discuss here several properties of minerals some of which related to:

- The interaction with visible light wavelengths, resulting in mineral colors, luster and streak (*optical properties*).
- The extent to which a mineral crystalcan be scratched, broken, splitted, attracted to magnet (*physical properties*).
- The reactivity degree of minerals with gases, acids, alkalis, organic molecules, dissolved salts and metals (*chemical properties*).

4.1. Optical properties:

Light is an electromagnetic vibration, but for the purpose of transmitted and reflected-light microscopy, it can be considered as being simply the transfer of energy by vibrating 'particles' along a path from the source to the observer. White light consists of many rays ranging in wavelength. White light consists of many rays ranging in wavelength, through the visible spectrum, from 380 nm to 770 nm.



4.1.1. Mineral Colors:

The observed mineral color results from absorption of some visible wavelengths and reflection the other ones, which appear for our eyes. For instance, the yellow colorof sulfur mineral is due to absorption of all visible wavelengths, with an exception for the yellow wavelength. The mineral color varies not only from mineral to another but also within the same mineral:

- *The color may be due to trace amounts of an atom in the crystal structure. For example, iron in quartz produces amethyst.*
- *The color effect may be produced by the inclusion of small particles of a different mineral of substance in the mineral, as with hematite inclusions in quartz, resulting in jasper.*

Most minerals that have a metallic luster vary little in color, but nonmetallic minerals can demonstrate wide variance. Although the color of a freshly broken surface of a metallic mineral is often highly diagnostic, this same mineral may become tarnished with time. Such tarnish may dull minerals such as galena (PbS), which has a bright bluish lead-gray colour on a fresh surface but may become dull upon long exposure to air. Bornite (Cu_5FeS_4), which on a freshly broken surface has a brownish bronze colour, may be so highly tarnished on an older surface that it shows variegated purples and blues. So, in the identification of minerals with a metallic lustre, it is important for the observer to have a freshly broken surface for accurate determination of colour.Many nonmetallic minerals have a relatively narrow range of colours, although some have an unusually wide range. Members of the plagioclase feldspar series range from almost pure white in albite through light gray to darker gray toward the anorthite end-member. Most common garnets show various shades of red to red-brown to brown.

Note: The color is a helpful property, but it cannot be considered a diagnostic feature for minerals; only specific minerals retain their characterized colors such as gold, malachite and turquoise.

4.1.2. Mineral Lustre:

METALLIC LUSTRE

NON-METALLIC LUSTRE

The term lustre refers to the general appearance of a mineral surface in reflected light. The main types of lustre, metallic and nonmetallic, are distinguished easily bythe human eye after some practice. ***Metallic*** refers to the lustre of an untarnished metallic surface such as gold, silver, copper, or steel. These materials are opaque to light; none passes through even at thin edges. Pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and galena (PbS) are common minerals that have metallic lustre. ***Nonmetallic lustre*** is generally exhibited by light-colored minerals that transmit light, either through thick portions or at least through their edges.The following terms are used to distinguish the lustre of nonmetallic minerals:

- ***Vitreous***, having the lustre of a piece of broken glass (this is commonly seen in quartz and many other nonmetallic minerals).
- ***Resinous***, having the lustre of a piece of resin (this is common in sphalerite [ZnS]).
- ***Pearly***, having the lustre of mother-of-pearl (i.e., an iridescent pearl-like lustre characteristic of mineral surfaces that are parallel to well-developed cleavage planes; the cleavage surface of talc [$Mg_3Si_4O_{10}(OH)_2$] may show pearly lustre).
- ***Greasy***, having the appearance of being covered with a thin layer of oil (such lustre results from the scattering of light by a microscopically rough surface.
- ***Silky***, descriptive of the lustre of a skein of silk or a piece of satin and characteristic of some minerals in fibrous aggregates (examples are fibrous gypsum [$CaSO_{42}H_2O$], known as satin spar, and chrysotile asbestos [$Mg_3Si_2O_5(OH)_4$].

4.1.3. Mineral Streak:

A mineral in powderform may have a different color from individual crystals. This can be considered an important feature for identification. It is not practical to crush minerals to identify them, so we use colorless porcelain plate which we scratch with the mineral. This method is only valid for minerals that are softer than the porcelain plate. The color of the streak is then observed, it can be similar to/ or different from the color mineral. The red-colored hematite gives red streak on scratching, while the brassy yellow-colored pyrite gives a black streak. Pyrite is also known as "fools gold" because it was mistaken for this naturally occurring precious metal, but gold has a yellow streak.

Streak (Cerat)

- Black - Graphite
- Black - Pryite
- Black - Magnetite
- Black - Chalcopyrite
- Gray - Galena
- Limonite - Yellow-brown
- Hematite - Red-brown

The red-brown streak of the mineral hematite

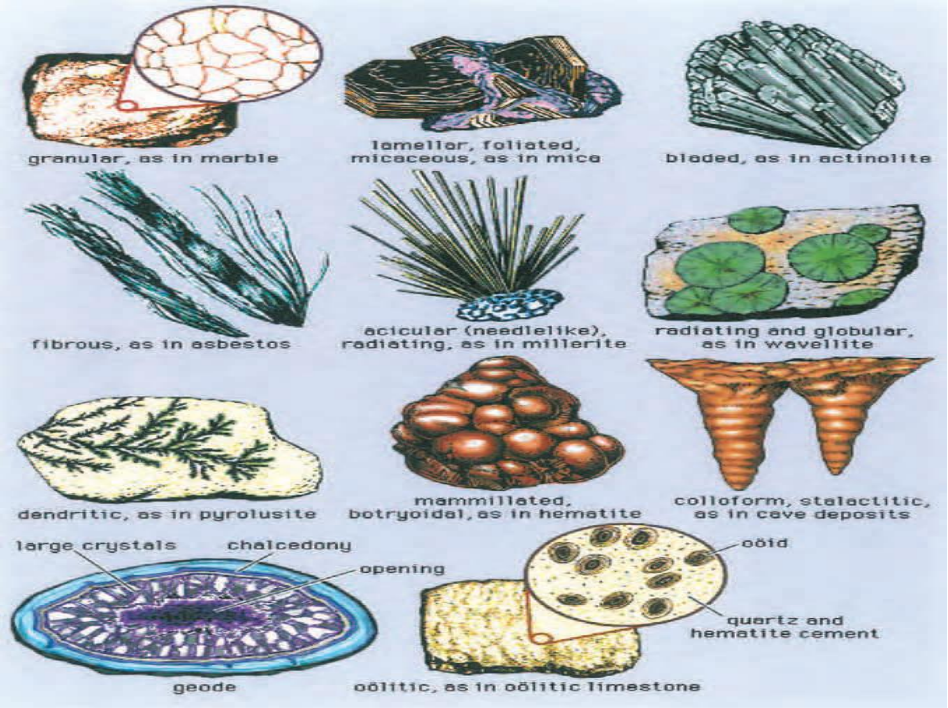
4.2. Physical Properties:

4.2.1 Crystal Habit and Crystal Aggregation

The majority of crystal occurrences are not part of well-formed single crystals but are found as crystals grown together in aggregates. Examples of some descriptive terms for such aggregations are given here:

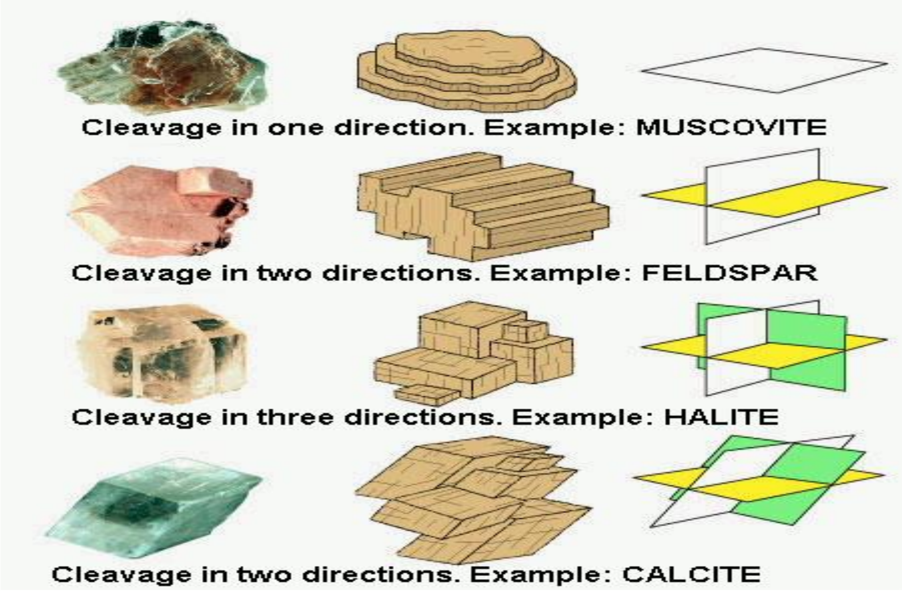
1. ***Granular***, an intergrowth of mineral grains of approximately the same size.
2. ***Lamellar***, flat, platelike individuals arranged in layers.
3. ***Bladed***, elongated crystals flattened like a knife blade.
4. ***Fibrous***, an aggregate of slender fibres, parallel or radiating.
5. ***Acicular***, slender, needlelike crystals.
6. ***Radiating***, individuals forming starlike or circular groups.
7. ***Globular***, radiating individuals forming small spherical or hemispherical groups.
8. ***Dendritic***, in slender divergent branches, somewhat plantlike.
9. ***Botryoidal***, globular forms resembling a bunch of grapes.
10. ***Colloform***, spherical forms composed of radiating individuals without regard to size (this includes botryoidal, reniform, and mammillary forms).
11. ***Stalactitic***, pendent cylinders or cones resembling icicles.

12. ***Concentric***, roughly spherical layers arranged about a common centre, as in agate and in geodes.
13. ***Geode***, a partially filled rock cavity lined by mineral material (geodes may be banded as in agate owing to successive depositions of material, and the inner surface is often covered with projecting crystals).
14. ***Oolitic***, an assemblage consisting of small spheres resemble fish roe.



4.2.2.Cleavage and Fracture

Both these properties represent the reaction of a mineral to an external force. Cleavage is breakage along planar surfaces, which are parallel to possible external faces on the crystal. It results from the tendency of some minerals to split in certain directions that are structurally weaker than others. Some crystals exhibit well-developed cleavage, as seen by the planar cleavage in mica; perfect cleavage of this sort is characterized by smooth, shiny surfaces. In other minerals, such as quartz, cleavage is absent. The cleavage of a specific mineral can be described by identifying the number of cleavage planes present through the mineral crystal. **For example,** gypsum contains one set of basal cleavage, while calcite is characterized by 3 cleavage directions.Cleavage directions of a crystal are consistent with its overall symmetry.

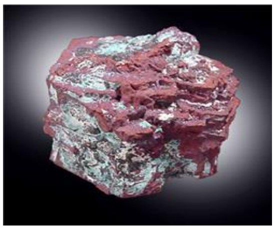


Some crystals do not usually break in any particular direction, reflecting roughly equal bond strengths throughout the crystal structure. Breakage in such minerals isknown as fracture. Three types of crystal fracture are recognized:

- The term ***Conchoidal***is used to describe fracture with smooth, curved surfaces that resemble the interior of a seashell; it is commonly observed in quartz and glass.

- ***Splintery*** fracture is breakage into elongated fragments like splinters of wood (e.g. all fibrous minerals).

- ***Hackly*** fracture is breakage along jagged surfaces (e.g. copper mineral).

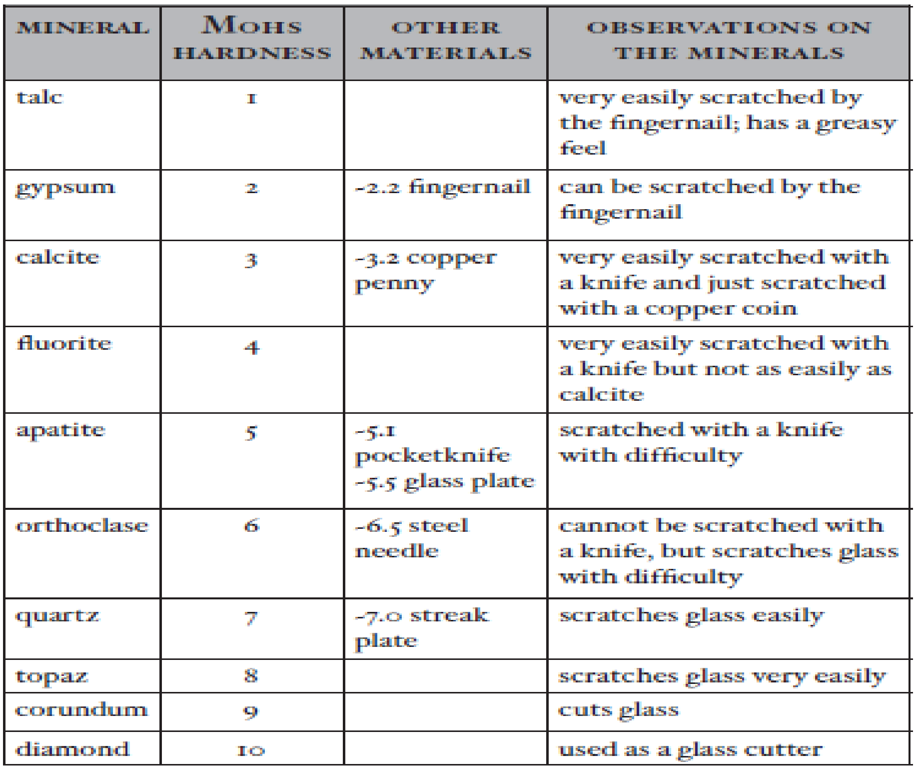


4.2.3 Hardness of Minerals

Hardness (H) is the resistance of a mineral to scratching. It is a property by which minerals may be described relative to a standard scale of 10 minerals known as the Mohs scale of hardness. The degree of hardness is determined by observing the comparative ease or difficulty with which one mineral is scratched by another or by a steel tool.For measuring the hardness of a mineral, several common objects that can be used for scratching are helpful, such as a fingernail, a copper coin, a steel pocketknife, glass plate or window glass, the steel of a needle, and a streak plate.

Because there is a general link between hardness and chemical composition, these generalizations can be made:

- Most hydrous minerals are relatively soft (H < 5).
- Halides, carbonates, sulfates, and phosphates also are relatively soft (H < 5½).
- Most sulfides are relatively soft (H < 5), with marcasite and pyrite being examples of exceptions (H < 6 to 6½).
- Most anhydrous oxides and silicates are hard (H > 5½).



MINERAL	MOHS HARDNESS	OTHER MATERIALS	OBSERVATIONS ON THE MINERALS
talc	1		very easily scratched by the fingernail; has a greasy feel
gypsum	2	-2.2 fingernail	can be scratched by the fingernail
calcite	3	-3.2 copper penny	very easily scratched with a knife and just scratched with a copper coin
fluorite	4		very easily scratched with a knife but not as easily as calcite
apatite	5	-5.1 pocketknife -5.5 glass plate	scratched with a knife with difficulty
orthoclase	6	-6.5 steel needle	cannot be scratched with a knife, but scratches glass with difficulty
quartz	7	-7.0 streak plate	scratches glass easily
topaz	8		scratches glass very easily
corundum	9		cuts glass
diamond	10		used as a glass cutter

4.2.4 Tenacity of Minerals

Several mineral properties that depend on the cohesive force between atoms (and ions) in mineral structures are grouped under tenacity. A mineral's tenacity can be described by the following terms:

- ***Malleable***, capable of being flattened under the blows of a hammer into thin sheets without breaking or crumbling into fragments (most of the native elements show various degrees of malleability, but particularly gold, silver, and copper).
- ***Sectile***, capable of being severed by the smooth cut of a knife (copper, silver, and gold are sectile).
- ***Ductile***, capable of being drawn into the form of a wire (gold, silver, and copper exhibit this property).
- ***Flexible***, bending easily and staying bent after the pressure is removed (talc is flexible).
- ***Brittle***, showing little or no resistance to breakage, and as such separating into fragments under the blow of a hammer or when cut by a knife (most silicate minerals are brittle).
- ***Elastic***, capable of being bent or pulled out of shape but returning to the original form when relieved (mica is elastic).

4.2.5Specific Gravity of Minerals

Specific gravity (G) is defined as the ratio between the weight of a substance and the weight of an equal volume of water. Since it is a ratio, specific gravity has no units. The specific gravity of a mineral depends on the atomic weights of all its constituent elements and the manner in which the atoms (and ions) are packed together. In mineral series whose species have essentially identical structures, those composed of elements with higher atomic weight have higher specific gravities. If two minerals (as in the two polymorphs of carbon, namely graphite and diamond) have the same chemical composition, the difference in specific gravity reflects variation in internal packing of the atoms or ions (diamond, with a G of 3.51, has a more densely packed structure than graphite, with a G of 2.23).

The specific gravity of unknown mineral can be determined in two ways:

1. ***The relative measurement:***By comparing with the known average specific gravity for non-metallic (2.65-2.75) and metallic minerals (around 5).
2. ***Using an accurate specific gravity balance:***An example of such an instrument is the Jolly balance, which provides numerical values for a small mineral specimen in air as well as in water). Such accurate measurements are highly diagnostic and can greatly aid in the identification of an unknown mineral sample.

4.2.6.Magnetism of Minerals

Ferromagnetic is a term that refers to materials that exhibit strong magnetic attraction when subjected to a magnetic field. Materials that show only a weak magnetic response in a strong applied magnetic field are known as paramagnetic. Those materials that are repelled by an applied magnetic force are known as diamagnetic. Because minerals display a wide range of slightly different magnetic properties, they can be separated from each other by an electromagnet. Such magnetic separation is a common procedure both in the laboratory and on a commercial scale.

4. 3.Chemical Properties of Minerals

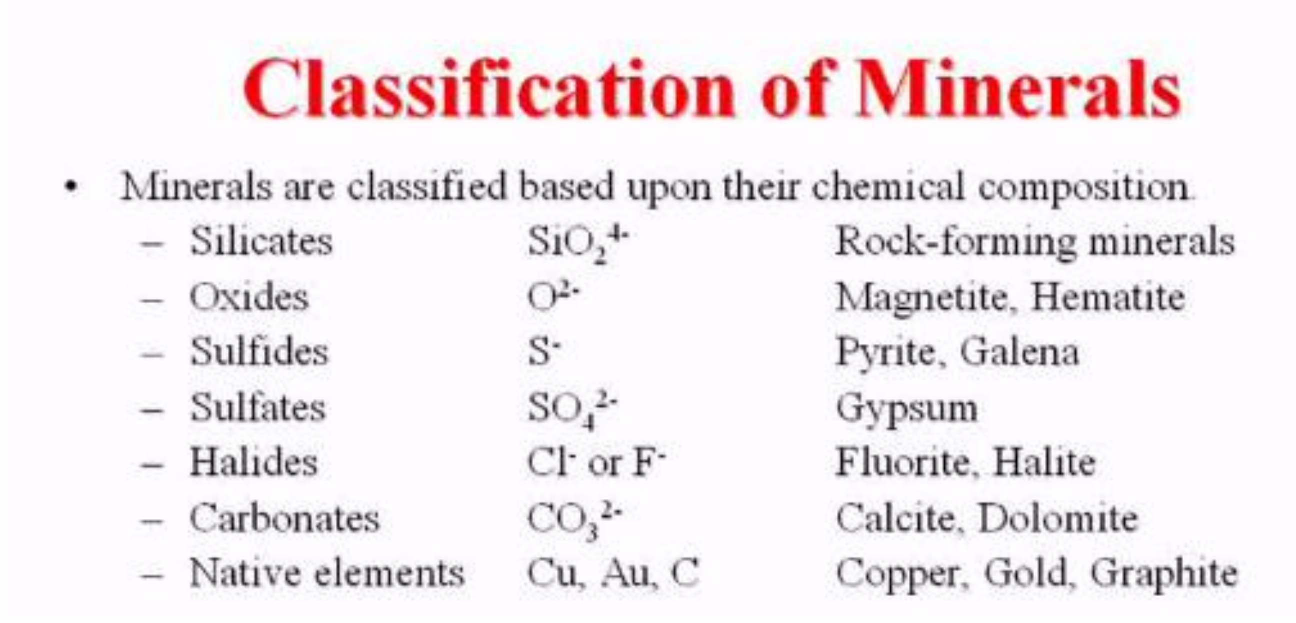
The chemical properties of minerals mean here the interaction of minerals with acids, which is considered as indication for the presence/absence of specific mineral phases. For instance,the positive identification of carbonate minerals is aided greatly by the fact that the carbon-oxygen bond of the CO_3 group in carbonates becomes unstable and breaksdown in the presence of hydrogen ions (H+) available in acids. This is expressed by the reaction: $2H^+ + (CO3)^{2-} \rightarrow H2O + CO_2$, which is the basis for the so-called **fizz test** with dilute hydrochloric acid (HCl). Calcite and aragonite as well as copper carbonates, show bubbling, or effervescence, when a drop of dilute hydrochloric acid is placed on the mineral. This “fizz” is due to the release of carbon dioxide (CO_2). Other carbonates such as dolomite, rhodochrosite, magnesite, and siderite will show slow effervescence when acid is applied to powdered minerals or moderate effervescence only in hot hydrochloric acid. From other perspective, the differential solubility degree of minerals in acids can be useful for separation of a given mineral from another. As such example, hematite can be separated from barite using HCl solutions due to the high acid resistance of barite.

Lecture#4: Classification of Minerals

5. Mineral Classification

Minerals are chemically classified into seven groups (silicates, oxides, sulfides, sulfates, halides, carbonates, and native) according to the associated anionic group rather than the dominant cation. This is attributed to two reasons:

1. Firstly, the similarities in properties of minerals with identical anionic groups are generally more pronounced than those with the same dominant cation. For example, carbonates have stronger resemblance to one another than do copper minerals.
2. Secondly, minerals that have identical dominant anions are likely to be found in the same or similar geologic environments. Therefore, sulfides tend to occur together in vein or replacement deposits.



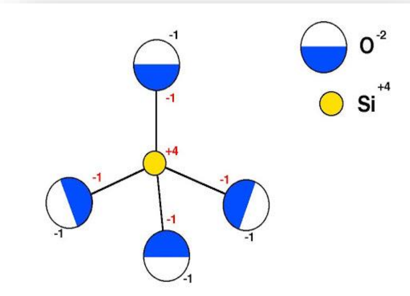
Classification of Minerals

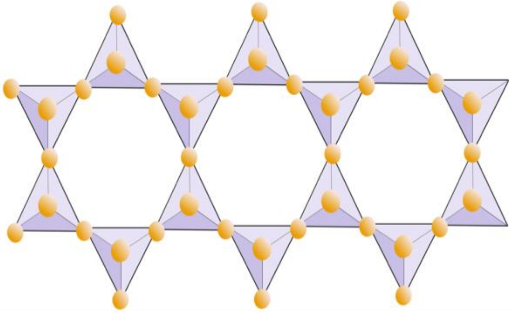
- Minerals are classified based upon their chemical composition

– Silicates	SiO_2^{4-}	Rock-forming minerals
– Oxides	O^{2-}	Magnetite, Hematite
– Sulfides	S^-	Pyrite, Galena
– Sulfates	SO_4^{2-}	Gypsum
– Halides	Cl^- or F^-	Fluorite, Halite
– Carbonates	CO_3^{2-}	Calcite, Dolomite
– Native elements	Cu, Au, C	Copper, Gold, Graphite

Silicates:

The silicates, owing to their abundance on the Earth, constitute the most important mineral class. Approximately 25 percent of all known minerals and 40 percent of the most common ones are silicates; the igneous rocks that make up more than 90 percent of the Earth’s crust are composed of virtually all silicates.The fundamental unit in all silicate structures is the silicon-oxygen $(SiO_4)^{4-}$ tetrahedron. It is composed of a central silicon cation (Si^{4+}) bonded to four oxygen atoms that are located at the corners of a regular tetrahedron. The positive charge (+4) of each silicon cation is satisfied by its four bonds to oxygen atoms. Each oxygen ion (O^{2-}), however, contributes only one-half of its total bonding energy to a silicon-oxygen bond, so it is capable of also bonding to the silicon cation of another tetrahedron. The SiO_4 tetrahedrons thereby become linked by shared oxygen atoms; this is referred to as polymerization. Besides silicon tetrahedral, aluminum can be surrounded with four oxygen atoms arranged tetrahedrally, but it can also occur in sixfold coordination with oxygen. The ability to maintain two roles within the silicate structure makes aluminum a unique constituent of these minerals. The tetrahedral AlO4 groups are approximately equal in size to SiO_4 groups and therefore can become incorporated into the silicate polymerization scheme. Aluminum in sixfold coordination may form ionic bonds with the SiO_4 tetrahedrons. Thus, aluminum may occupy tetrahedral sites as a replacement for silicon and octahedral sites in solid solution with elements such as magnesium and ferrous iron.Octahedral sheets are composed of individual octahedrons that share edges composed of oxygen and hydroxyl anion groups with Al, Mg, Fe3+ and Fe2+ typically serving as the coordinating cation. These octahedrons too, are arranged in a hexagonal pattern.





Oxides and Hydroxides:

These classes consist of oxygen-bearing minerals; the oxides combine oxygen with one or more metals, while the hydroxides are characterized by hydroxyl $(OH)^-$

groups.The oxides are further divided into two main types: simple and multiple. Simple oxides contain a single metal combined with oxygen in one of several possible metal:oxygen ratios (X:O): XO, X_2O, X_2O_3, etc. Ice, H2O, is a simple oxide of the X_2O type that incorporates hydrogen as the cation. Multiple oxides consist of two metals attached to oxygen atoms (e.g. Ilmenite $TiFeO_3$). Oxide minerals generally display strong ionic bonding. They are relatively hard, dense, and refractory.Oxides minerals generally occur in small amounts in igneous and metamorphic rocks and also as preexisting grains in sedimentary rocks. Several oxides have greateconomic value, including the principal ores of iron (hematite and magnetite), chromium (chromite), manganese (pyrolusite, as well as the hydroxides, manganite and romanechite), tin (cassiterite), and uranium (uraninite).

The $(OH)^-$ group of the hydroxides generally results in structures with lower bond strengths than in the oxide minerals. The hydroxide minerals tend to be less densethan the oxides and also are not as hard. All hydroxides form at low temperatures and are found predominantly as weathering products, as, for example, from alteration in hydrothermal veins. Some common hydroxides are brucite [Mg(OH)2], manganite [MnO· OH], diaspore [α-AlO· OH], and goethite [α-FeO· OH]. The ore ofaluminum, bauxite, consists of a mixture of diaspore, boehmite (γ-AlO·OH—a polymorph of diaspore), and gibbsite [Al(OH)3], plus iron oxides. Goethite is a common alteration product of iron-rich occurrences and is an iron ore in some localities.

Sulfides:

This important class includes most of the ore minerals. Sulfide minerals consist of one or more metals combined with sulfur. Sulfides are generally opaque and exhibit distinguishing colors and streaks (e.g. pyrite, chalcopyrite, galena, Sphalerite, covellite..etc). The non-opaque varieties (e.g., cinnabar) possess transmitting light only on the thin edges of a specimen.

Sulfates:

This class is composed of a large number of minerals, but relatively few are common. The most frequently occurring sulfates are anhydrite, gypsum, and members of the barite group (barite and anglesite). All contain anionic $(SO_4)^{2-}$ groups in their structures. These anionic complexes are formed through the tight bonding of a central S^{6+} ion to four neighbouring oxygen atoms in a tetrahedral arrangement around the sulfur.This closely knit group is incapable of sharing any of its apical oxygen atoms with other SO_4 groups; as such the tetrahedrons occur as individual, unlinked groups in sulfate mineral structures.

Halides:

Members of this class are distinguished by the large-sized anions of the halogens chlorine, bromine, iodine, and fluorine. The ions carry a charge of negative one, and when associated with rather large, weakly polarizing cations of low charge, such as those of the alkali metals, both anions and cationsform ionic bonds (e.g. halite, fluorite). These halides manifest relatively low hardness and moderate-to-high melting points. In the solid state they are poor thermal and electric conductors, but when molten they conduct electricity well.

Carbonates:

The carbonate minerals contain the anionic complex (CO3)2-, which is triangular in its coordination—i.e., with a carbon atom at the centre 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 carbonates are divided into three groups that differ in structure type: calcite, aragonite, and dolomite. Members of the calcite group exhibit perfect rhombohedral cleavage. 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.Dolomite [$CaMg(CO_3)_2$] and ankerite [$CaFe(CO_3)_2$] are main members of the dolomite group. The dolomite structure can be considered as a calcite-type structure in which magnesium and calcium cations occupy the metal sites in alternate layers. The calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions differ in size by 33 percent, and this produces cation ordering with the two cations occupying specific and separate levels in the structure. Dolomite has a calcium-to-magnesium ratio of approximately 1:1, which gives it a composition intermediate between $CaCO_3$ and $MgCO_3$.The copper carbonates azurite and malachite are the only notable hydrous varieties.

Native elements:

A native element is a chemical element that may occur in nature uncombined with other elements. The group of native elements does not include those that occur as atmospheric gasses, however.These native elements are commonly divided into three groups—namely, metals (platinum, iridium, osmium, iron, zinc, tin, gold, silver, copper, mercury, lead, chromium); semimetals (bismuth, antimony, arsenic, tellurium, selenium); and nonmetals (sulfur, carbon).

Questions to be answered

-Although gold is characterized by native nature, it can react with cyanide during gold extraction, why?????????

-Sulfate minerals are difficult to be solved in sulfuric acid, why?????

Lecture#5: Mineral-Forming Processes- Igneous Processes

Mineral-Forming Processes: An introduction

Mineral deposits form because some medium serves as a concentrating and transporting agent for the ore minerals, and some process subsequently causes the transporting agent to precipitate, or deposit, the minerals. Examples of concentrating and transporting agents are groundwater, seawater, and magma; examples of precipitating processes are boiling (as in a hot spring), the cooling of a hot Solution, the crystallization of a magma, and a chemical reaction between a solution and the rocks through which it flows. The same kinds of concentrating and transporting a gent and the same kinds of precipitating process are involved in the formation of deposits of both geochemically abundant and geochemically scarce metals. We will discuss **three main mineral-forming processes:**

- Igneous/or magmatic Processes
- Hydrothermal Processes
- Sedimentary Processes

1. Igneous Processes:

Magma is a hot molten rock materials resulting from partial melting of the upper mantle rocks. When rocks undergo melting, their solid mineral components are converted into a homogeneous liquid phase rich in all chemical elements, which were once time the main structural units of the molten minerals.

Ore minerals can be formed by concentration of specific elements from magma. These elements originally occur as trace elements (e.g. Cu, Ni, Cr and W whose content is lower than 0.1wt%) in different rock types.

When rocks undergo partial melting, trace elements partition themselves between the melt phase and solid residue. Those that prefer the solid are referred to as compatible (i.e. they have an affinity with elements making up the crystal lattice of an existing mineral), whereas those whose preference is the melt are termed incompatible. Likewise, during cooling and solidification of magma, compatible elements are preferentially taken up in the crystals, whereas incompatible elements are enriched in the residual melt. Enrichment of trace elements and potential ore formation can, therefore, be linked to the concentration of incompatible elements in the early melt phase of a rock, or the residual magma during progressive crystallization. Compatible trace elements tend to be “locked up” in early formed rock-forming minerals and are typically not concentrated efficiently enough to form viable ore grade material.

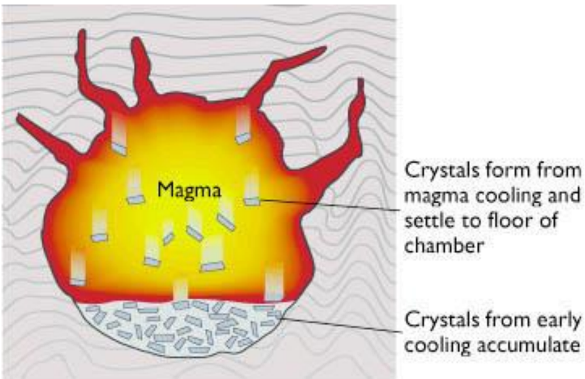
In general, minerals are crystallized from magma by what so-called **magmatic segregation**. This refers to any process by which one or more minerals become locally concentrated (segregated) during the cooling and crystallization of magma. Rocks formed as a result of magmatic segregation is called magmatic cumulate. While magma may start as a homogeneous liquid, magmatic segregation during crystallization can produce an assemblage of cumulates with widely differing compositions. Extreme segregation can sometimes produce monomineraliccumulates; a dramatic example occurs in the Bushveld Igneous Complex of South Africa, where cumulus layers of chromite (iron-magnesium-chromium oxide, the only chromium ore mineral) are encased in cumulus layers of anorthite (calcium-rich feldspar).Mineral deposits that are magmatic cumulates are only found in mafic and ultramafic igneous rocks (i.e., rocks that are low in silica). This is due to the control exerted by silica on the viscosity of magma: the higher the silica content, the more viscous magma and the more slowly segregation can proceed. Highly viscous magmas, such as those of granitic composition, tend to cool and crystallize faster than segregation can proceed. In low silica (and, hence, low-viscosity) magmas such as gabbro, basalt, and komatiite, mineral grains can float, sink, or be moved so rapidly by flowing magma that segregation can occur before crystallization is complete. Two main mechanisms by which minerals are directly segregated from magma:

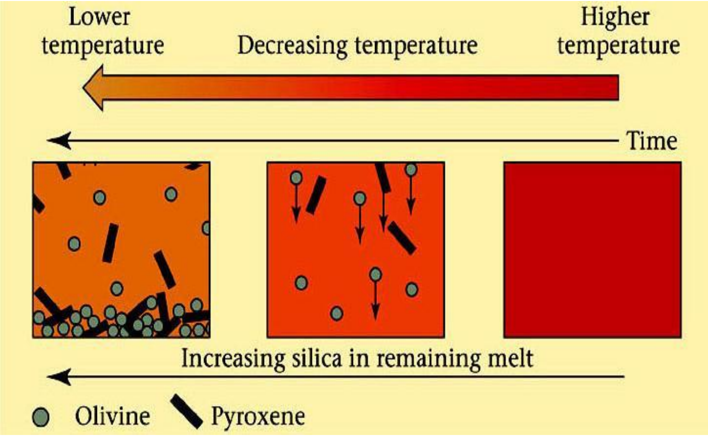
a. Fractional Crystallization:

Fractional crystallization can be defined as all mechanical processes by which early formed crystals are prevented from equilibrium with the melt from which they grow. There are three ways to achieve this separation:

1. Gravitational Separation:

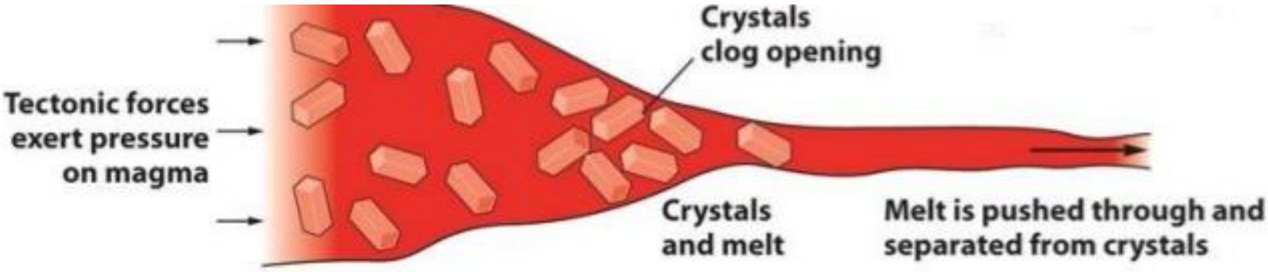
If crystals differ in density from the surrounding liquid, they may rise or sink down to the bottom of magmatic hearths. The liquid will be progressively depleted in the components that taken by the crystalline phases, and layered series of igneous rocks may form.





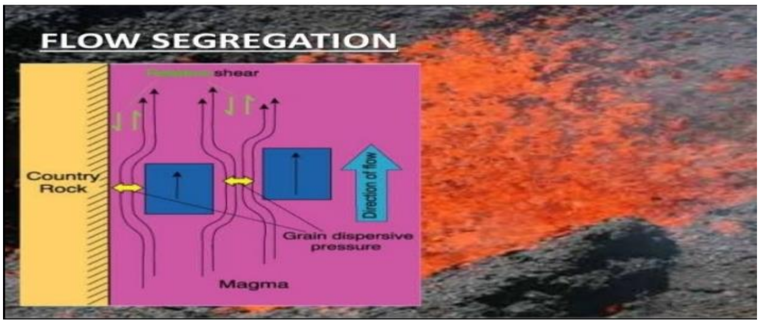
2. Filter Pressing:

A process of magmatic differentiation wherein a magma having crystallized to mush of interlocking crystals in liquid is compressed by earth movement and the liquid moves toward regions of lower pressure, thus becoming separated from the crystals.



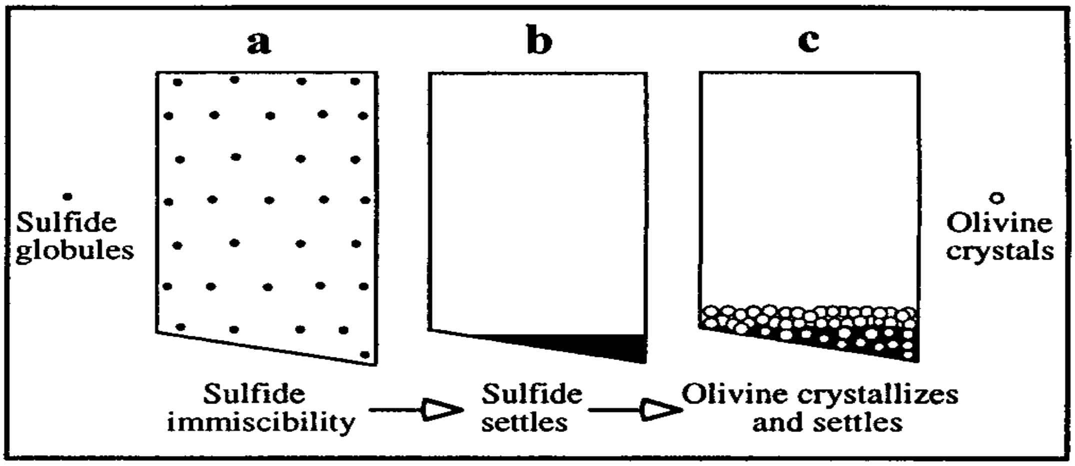
3. Flow Differentiation:

As magma moves through a conduit, friction establishes a velocity gradient such asthe central portion of the magma flows faster than the marginal parts. The suspended crystals tend to be concentrated in the high velocity zone of a magma that is moving by laminar flow.



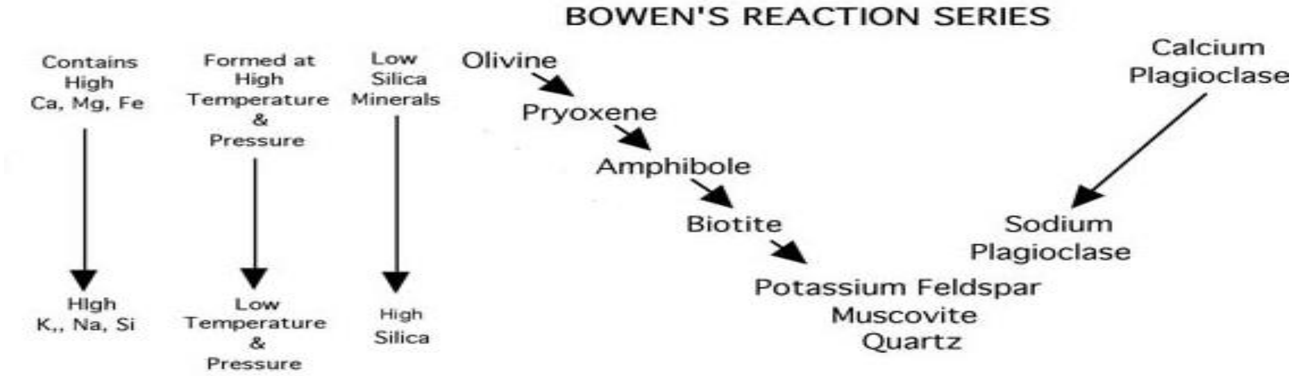
b. Liquation "immiscible melts:

A different kind of magmatic segregation involves liquid immiscibility. A cooling magma will sometimes precipitate droplets of a second magma that has an entirely different composition. Like oil and water, the two magmas will not mix (i.e., they are immiscible). The chemical principle governing precipitation of an immiscible liquid is the same as that governing crystallization of a mineral from magma: when the concentration of a particular mineral within parent magma reaches saturation, precipitation occurs. If saturation is reached at a temperature above the melting point of the mineral, a drop of liquid precipitates instead of a mineral grain. The composition of this immiscible drop is not exactly that of the pure mineral, because the liquid tends to scavenge and concentrate many elements from the parent magma, and this process can lead to rich ore deposits.Iron sulfide is the principal constituent of most immiscible magmas, and the metals scavenged by iron sulfide liquid are copper, nickel, and the platinum group. Immiscible sulfide drops can become segregated and form immiscible magma layers in a magma chamber in the same way that cumulus layers form; then, when layers of sulfide magma cool and crystallize, the result is a deposit of ore minerals of copper, nickel, and platinum-group metals in a gangue of an iron sulfide mineral.



Crystallization Sequence of Minerals:

Minerals crystallize from magma through a specific sequence called ***Bowen's reaction series***.Bowen demonstrated that it was technically possible o produce a sequence of minerals from a single magma source through cooling and fractionation. He further found hat here are two sequences of minerals, he discontinuous reaction series and the continuous reaction series.



1. Discontinuous Reaction Series:

It constitutes the left side of Bowen's reaction series. These are a group of mafic or iron magnesium bearing minerals–olivine, pyroxene, amphibole, and biotite .if the chemistry of the melt is correct, these minerals react discontinuously to form the next mineral in the series. In a basaltic melt, olivine will be he firs mafic mineral to form. When the temperature is low enough to form pyroxene, all of the olivine will react with he melt to form pyroxene and pyroxene will crystallize out of he melt. At he crystallization temperature of amphibole, all the pyroxene will react with the melt to form amphibole that crystallize. At the crystallization temperature of biotite, all of the amphibole will react to form biotite and biotite will crystallize. Thus all igneous rocks should only have biotite, but we know that is no rue. If you are crystallizing olivine and there is not enough silica to form pyroxene, then the reaction will no occur and olivine will remain.

2. Continuous Reaction Series:

It comprises the right hand side of Bowen's reaction series. They are plagioclase minerals that whose formula (Ca, Na) (Al, Si)3O8. The highest temperature plagioclase has only calcium (Ca). The lowest temperature plagioclase has only sodium (Na). In between, these ions mix in a continuous series from 100% Ca and 0 % Na at highest temperature to 50 % Ca and 50% Na at the middle temperature to 0 % Ca and 100 % Na at the lowest temperature.

Note: the difference between the continuous and discontinuous reaction series is represented by the continuous occurrence of homogenous solid solution along the plagioclase series, while the solid solution occurs only within each mineral group of the discontinuous sequence.

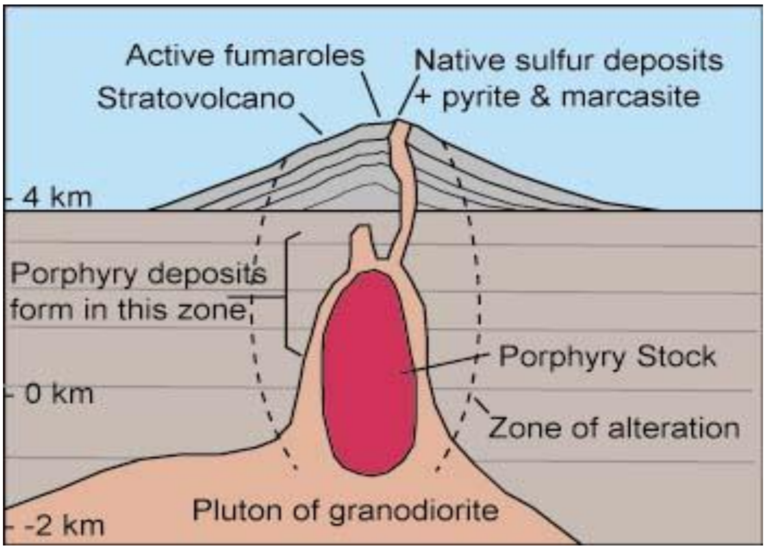
Lecture#6: Mineral-Forming Processes-Hydrothermal Processes

Hydrothermal Processes: An Introduction

Hydrothermal solutions are considered the main source of the major ore deposits. They are hot brine solutions capable of dissolving, transporting, and concentrating various precious deposits (e.g. sulphides, oxides, Au, and Cu). The salinity of hydrothermal solutions comes from the occurrence of sodium-calcium chlorides with additions of magnesium and potassium salts. The solutions range in concentration from varies from few percent to 50wt% of the dissolved solids. Four sources are suggested for the origin of such solutions:

- **Magmatic water:**

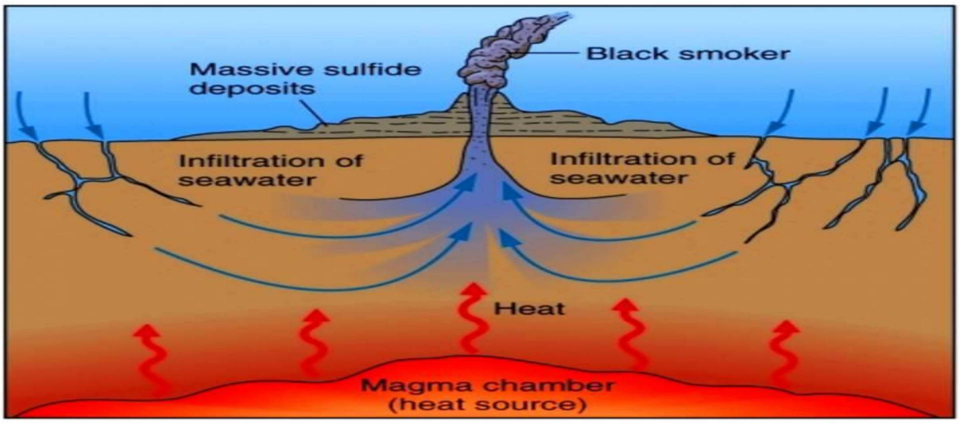
This type of water is mainly incorporated into magma during the dehydration and melting of the hydrous silicate minerals (e.g.biotite, muscovite and hornblende) and its solubility in the molten rocks is strongly pressure dependent. The amount of hydrothermal fluids that will be exsolved from a magma depends on its initial water content (2.5-6wt% H_2O), its depths of emplacement, and its crystallization history. When an ascending water-bearing magma begins to crystallize, the volume of the residual magma becomes smaller and smaller, and H_2O (with other volatiles and precious incompatible metals) is concentrated in this decreasing volume and expelled through the fractured country rocks as metals-bearing hydrothermal solutions (e.g. porphyry copper deposits associated with the intrusive porphyry granite).



- **Meteoric water (lakes, rivers, rainfall, groundwater, and seawater):**

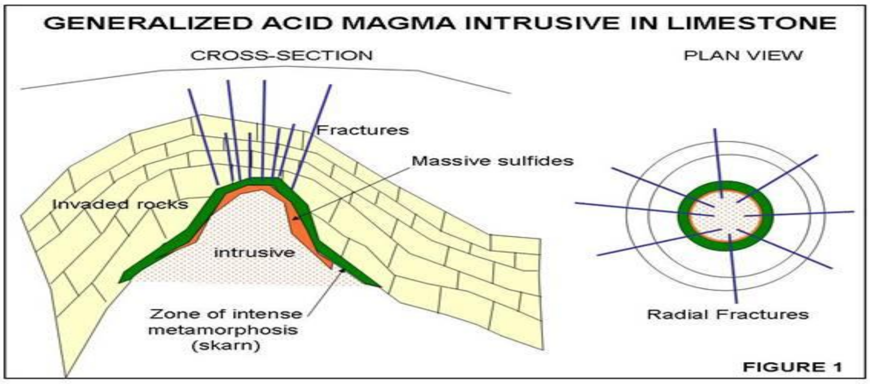
Meteoric water can penetrate downward through fractures and faults where temperature gradually increases, and hence more and more metals can be leached from the surrounding rocks. Quartz is also leached by brine solutions at 900 C, and occurs as H_4SiO_4 which is a typical constituent of hydrothermal solutions and explain the common occurrence of quartz in the hydrothermal veins.

For example, seawater can be circulated through the oceanic crust. It is percolated down through numerous faults and weak zones in the oceanic crust (e.g. mid ocean rides).Its temperature increases at closer contact with igneous intrusion, which makes it a powerful solvent capable of leaching several metals (e.g. Pb, Zn, Ag) from the country rocks. Once it ascends upward, black smokers are formed due to the rapid cooling of the hot metal-bearing solutions.



- **Metamorphic water:**

This type is produced by metamorphic hydration reactions. As such example, When a limestone or marble is invaded by a high-temperature hydrothermal solution, the carbonate minerals calcite and dolomite react strongly with the slightly acid solution to form a class of mineral deposit called a Skarns. Because solutions tend to have high temperatures close to a magma chamber, most Skarns are found immediately adjacent to intrusive igneous rocks. The solutions introduce silica and iron, which combine with the calcium and magnesium in the parent rock to form silicate minerals such as diopside, tremolite, and andradite. The hydrothermal solutions may also deposit ore minerals of iron, copper, zinc, tungsten, or molybdenum.



- **Connate water:**

Formational water trapped in the pores of sediments deposited in aquous environments.

There are three principal types of hydrothermal deposits:

a) **Hypothermal Mineral Deposits**: refer to the high temperature deposits ranging from about 300 to 500 ^{o}C. These deposits are formed at great depth under high pressure and sometimes referred to as deep-seated deposits. These deposits are characterized by gangue minerals (unwanted minerals with which ore minerals usually intergrowth) such as garnet, biotite, hornblende, pyroxene, magnetite, tourmaline, all of them being associated with quartz. The chief metals extracted from such deposits are tin, tungsten, gold, copper, molybdenum, and lead.

b) Mesothermal Mineral Deposits: are formed under intermediate temperatures (300-200 ºC) and generally at depths under high pressure. The chief meals mined along with other ore minerals are gold, silver, lead, and copper, zinc .

c) Epithermal Mineral Deposits: constitute the third group which formed at moderate temperatures, probably rarely exceeding 150 ºC and many of them are developed close the surface. The chief meals found in these deposits are gold, silver, and mercury along with other ore minerals.

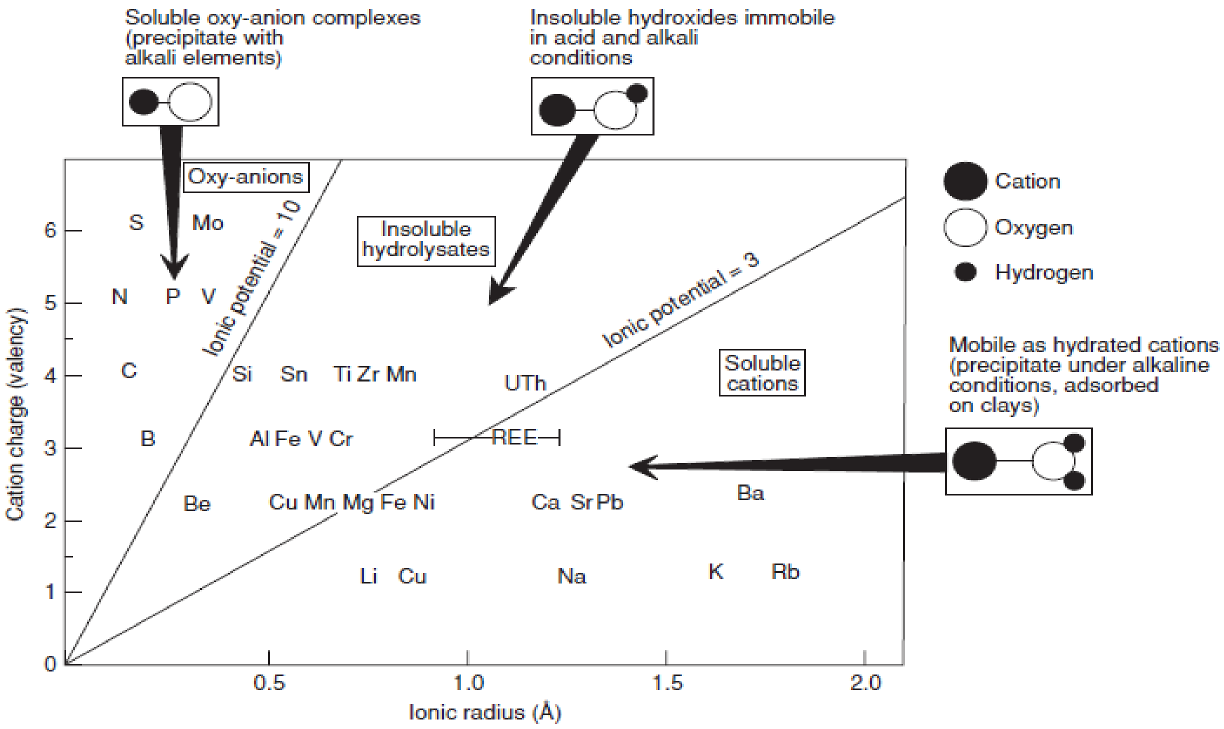
Lecture#7: Mineral-Forming Processes-Sedimentary Processes

6.3. Sedimentary/Surficial Processes:

The surficial mineral-forming processes result from the chemical weathering of re-existing materials and evaporation followed chemical precipitation. Many different metals are enriched in the surficial environment, the most important ofwhichinclude Al, Ni, Mn, Fe, Cu, Au, Pt, and U.**The chemical weathering processes include:**

- **Dissolution and hydration:**

Dissolution is a chemical process in which the solid naturally occurring materials are converted into a liquid phase. Certain natural materials such as halite (NaCl) and other evaporitic minerals ($CaCl_2$), as well as the carbonate minerals (calcite, siderite, dolomite, etc.), tend to dissolve relatively easily and completely in normal to acidic groundwaters and precipitate again either on evaporation or under alkaline conditions. The solubility of elements is a function of its ionic potential (ionic charge/ionic radius). Cations with ionic potential<3 are soluble under normal-acidic conditions and precipitate under alkaline conditions. Anions of ionic potential > 10 form soluble complexes that precipitate with alkalis. Ions with intermediate values (ionic potentials between 3 and 10) tend to be relatively insoluble and precipitate readily as hydroxides.



Over the pH range at which most groundwaters exist (5–9), silicon is more soluble than aluminum and consequently chemical weathering will tend to leach Si, leaving behind a residual concentration of immobile Al and ferric oxides/ hydroxides. This is typical of soil formation processesein tropical, high rainfall areas and yieldslateritic soil profiles, which can also contain concentrations of bauxite (aluminum ore) and Ni. Lateritic soils will not, however, form under acidic conditions ($pH < 5$) as Al is more soluble than Si and the resultant soils are silica-enriched and typically depleted in Al and Fe. On the other hand, hydration of minerals can occur directly, good examples of which include the formation of gypsum ($CaSO_4.2H_2O$) from anhydrite ($CaSO_4$) and the incorporation of water into the structure of clays such as montmorillonite.

- **Hydrolysis:**

Hydrolysis is defined as a chemical reaction in which one or both of the O–H bonds in the water molecule is broken. Such reactions are important in weathering. One example occurs during the breakdown of aluminosilicate minerals such as feldspar, and also the liberation of silicon as silicic acid into solution, as shown by the reaction: $Si^{4+} + 4H_2O \Leftrightarrow H_4SiO_4 + 4H^+$

Another example relates to the hydrolysate elements such as Fe and Al that are relatively soluble in acidic solutions, but will precipitate as a result of hydrolysis. The hydrolysis of aluminum, yielding an aluminum hydroxide precipitate, is illustrated by reaction: $Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_3 + 3H^+$

- **Oxidation-reduction:**

Oxidation (and reduction) refers essentially to chemical processes that involve the transfer of electrons. In the surficial environment oxygen, present in either water or the air, is the most common oxidizing agent. The element most commonly oxidized in the surficial environment is probably iron, which is converted from the ferrous (Fe^{2+}) to the ferric (Fe^{3+}) valence state by oxidation (loss of electrons). An example of the role of oxidation in chemical weathering is provided by the relative instability of biotite compared to muscovite. Biotite has the formula $K^+[(Mg^{2+}, Fe^{2+})_3(Si_3Al)O10(OH)_2]^-$ and is much more easily weathered than muscovite $K^+[(Al_2)(Si_3Al)O_{10}(OH)_2]^-$ because of the ease with which the ferrous iron can be oxidized to ferric iron. Weathering and the resulting oxidation of Fe in biotite leads to a charge imbalance that destabilizes the mineral, a process that is less likely to happen in muscovite since it contains no iron in its lattice. The presence of iron in minerals such as olivine and the orthopyroxenes is one of the main reasons why they are so unstable in the weathering zone.

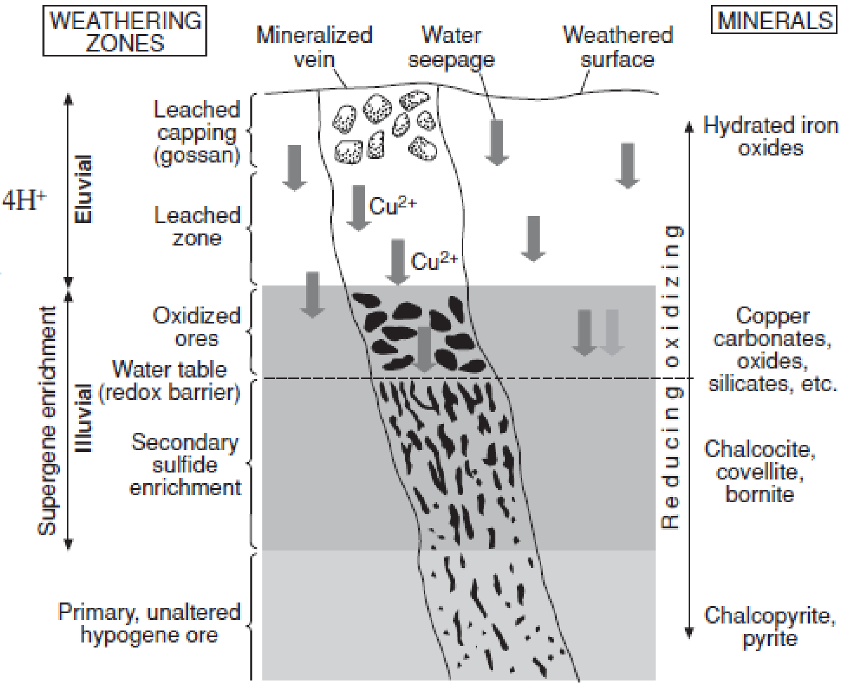
Besides mineral destabilization, the oxidation process can result in mineral formation. As such example, the oxidation –hydration processes of the glauconite deposits at El-Bahariya Oasis have participated in the formation of El-Gedida iron deposits. This was occurred by the oxidation of ferrous iron in glauconite structure and leaching different proportions of the other elements (e.g. Si, Al, Mn, Ca, Mg…..etc) under oxidized, acidic humid conditions.

Oxidation-reduction reactions can also lead to form ore minerals (e.g. Cu minerals) through what ***so-called super-gene enrichment*** in which the primary Cu minerals (e.g. chalcopyrite) are oxidized and leached downward by the action of oxidized, acidic groundwater, and then the soluble cuprous and sulfate ions are reduced and precipitated below the water table as secondary Cu minerals (e.g. chalcocite, covellite, and bornite). The residual layer in the upper weathering profile is enriched in iron oxyhydroxides (e.g. hematite and goethite) and called ***gossan***.

$$\underset{\text{chalcopyrite}}{4CuFeS_2} + 17O_2 + 10H_2O \Rightarrow \underset{\text{goethite}}{4Fe(OH)_3} + 4Cu^{2+} + 8SO_4^{2-} + 8H^+$$

$$2FeS_2 + 2H_2O + 7O_2 \Leftrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

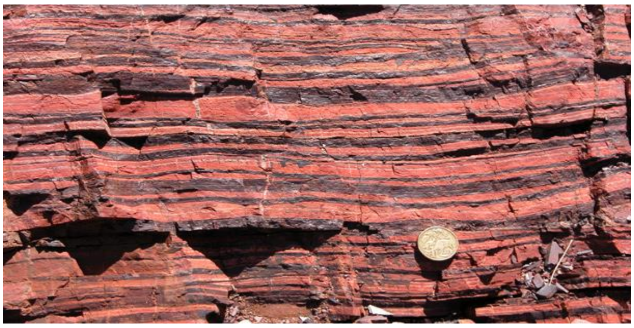
$$2Fe^{2+} + 3H_2O + O_2 \Leftrightarrow \underset{\text{goethite}}{2FeOOH} + 4H^+$$



Chemical Precipitation of Minerals:

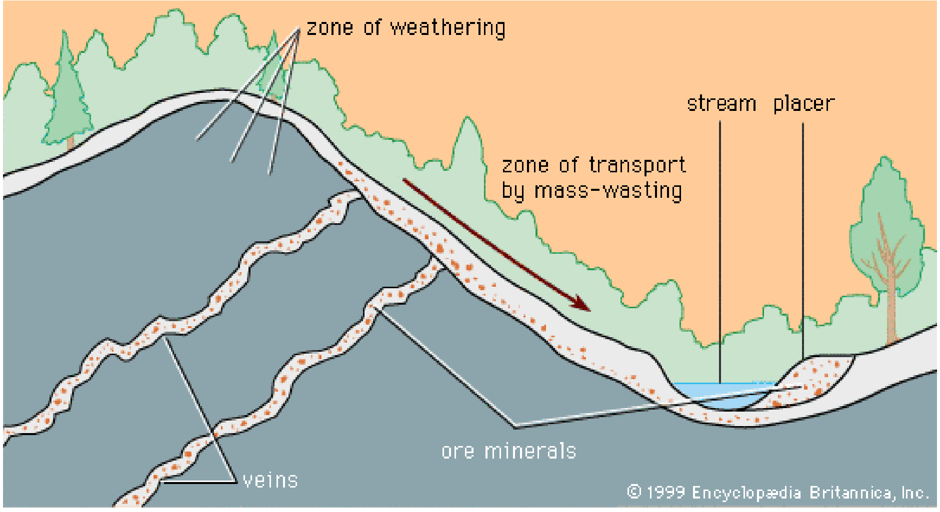
In addition to chemical weathering, minerals can also be crystallized by the chemical precipitation from seawater. When either sea or lake waters evaporate, salts are precipitated. These salts include <u>sodium chloride, potassium and magnesium chlorides, borax, and sodium carbonate</u>. Such salts are important economically. There is another mineral type chemically precipitated from seawater, ***it is a banded iron***

formation (BIF), so called because they are finely layered alternations of cherty silica and an iron mineral, generally hematite, magnetite, or siderite. It was formed by the action between iron dissolved in seawater and oxygen released by the photosynthetic cyanobacteria (2.1 billion y. ago).



Placer Deposits:

When mineral grains of different density are moved by flowing water, the less dense grains will be most rapidly moved, and a separation of high density and low density grains can be effected. Mineral deposits formed as a result of gravity separation based on density are called placer deposits.For effective concentration , placer minerals must not only have a high density (greater than about 3.3 gm/cm^3 , they must also possess a high degree of chemical resistance to dissolution or reaction with surface water and be mechanically durable. The common sulfide ore minerals don't form placers, because they rapidly oxidize and break down. Ore minerals having suitable properties for forming placers are the oxides cassiterite (tin), chromite (chrome), ilmenite and rutile (titanium). In addition, native gold and platinum and diamond have been mined from placers.



Lecture#8: Industrial Minerals and their Usage-Fe, Mn, and Ti-minerals

Industrial Minerals and Their Use: An Introduction

The term ***industrial minerals***refer to both metallic and non-metallic minerals that have a wide range of industrial applications. Within the following lines, we will discuss some important industrial minerals (Fe-minerals, Mn-minerals, ilmenite, barite, glauconite, clay minerals, calcium carbonate-minerals, feldspar, and asbestos) in terms of *origin, pre-treatment & beneficiation, and industrial applications*.

Iron-Minerals:

Hematite: Fe_2O_3

Limonite / Goethite: $Fe_2O_3.H_2O$

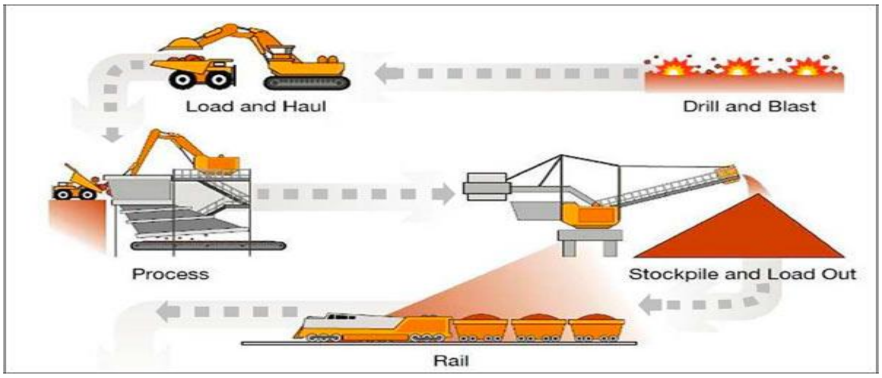
Magnetite: Fe_3O_4

Magmatic processes: Fractional crystallization at the early stages of magma cooling (e.g. magnetite).

Hydrothermal processes: Direct precipitation from Fe-bearing hydrothermal solutions (e.g. hematite).

Sedimentary processes: Direct precipitation from seawater (e.g. BIF), or the chemical weathering of specific minerals (e.g. glauconite).

- **Pre-treatment & Beneficiation Processes:**

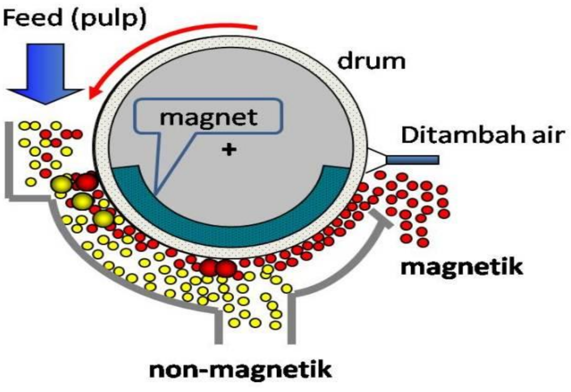


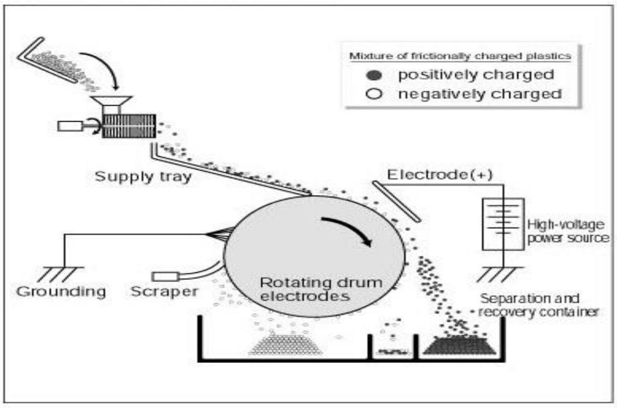
The run-off mine iron deposits are firstly subjected to pre-treatment processes that comprise comminution (crushing & grinding) and sieving. If the ground ore contain high levels of impurities (e.g. silica, barite, and Mn minerals), specific beneficiation methods (e.g. gravity, magnetic, and electrostatic separation as well as hydro- and bio-metallurgy) are required here prior to the industrialization step. For example, there is about one million ton of the baritic iron ore (proved and probable reserves) mostly concentrated in the high central area of El-Gedida mine area. BaO content in this area reaches up to 34wt%, which is more than the allowable limit (3wt%) for the steel production.

The high percentage of BaO present in the iron ore is considered one of the problems which face the production of pig iron in the blast furnace at Helwan. Increasing BaOcontent makes:

- The reduction process more energy consumption due to the high thermal stability of barite (1580°C).
- The undesirable barium content decreases the quality of the produced pig iron.

Barium, represented by barite, can be separated from iron minerals by dry-high intensity magnetic separation, wet-low intensity magnetic separation after adequate roasting (the transformation of hematite into magnetite) by coke, electrostatic separation, and chemical leaching of iron using HCl solution.





Chemical specifications required for the production of iron and steel at

Fe	SiO_2	MnO	BaO	Cl
52%+/-1	7.5%	2-4%	3%	0.7

- **Industrial application:**

Magnetite, hematite and limonite are the main feed materials for the production of iron and steel after proper pre-treatment and beneficiation processes. The pre-treated ore is well mixed with suitable quantities of coke "reductant", also proper amount of lime is added into furnace charge to interact and collect the resultant slag that is composed mainly of silica, alumina, calcium, and barium.

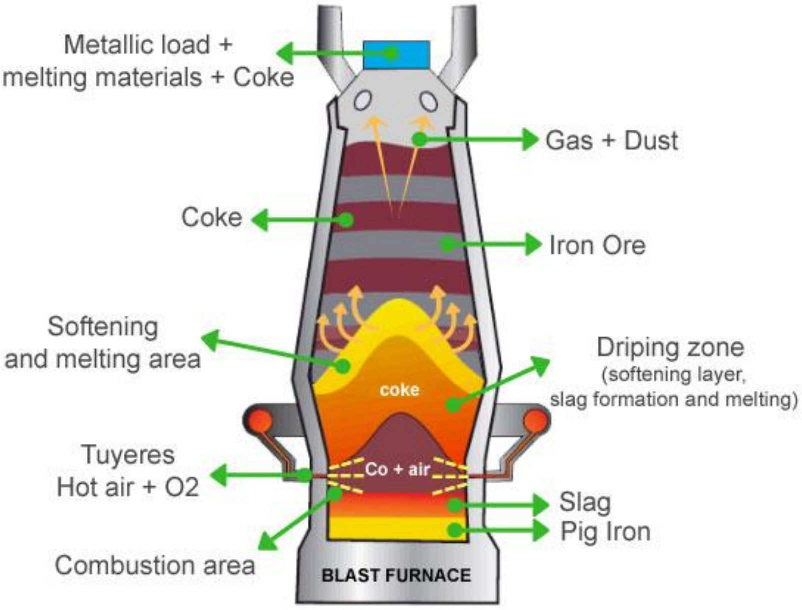


Figure 1 - Blast Furnace Operation

Mn-Minerals:

Pyrolusite: MnO_2

Cryptomelane: $[K (Mn^{+4}, Mn^{+2})_8O_{10}]$

Rhodochrosite: $(MnCO_3)$

- **Origin:**

Mn-minerals are originated from the hydrothermal solutions, the chemical weathering of pre-existing Mn oxides (e.g. super-gene enrichment of cryptomelane), and the direct precipitation from seawater (Um BogmaMn deposits, Sinai).

- **Pre-treatment & Beneficiation Processes:**

Mn deposits are undergone size reduction and probably magnetic separation to eliminate the associate gangues (e.g. barite, calcite, gypsum, and dolomite).

- **Industrial application:**

Manganese is required in the form of ferromanganese alloys for iron and steel industry by

- Virtue of its sulfur-fixing that prevents the formation of a liquid iron sulfide at the grain boundaries.
- Deoxidizing agent and alloying properties.

In order to reduce the continuous consumption of the high-grade ores, manganese high-grade ores can be mixed with low-grade counterparts to obtain a suitable blend for ferromanganese alloys production. One such example is blending the high-grade Um Bogma Mnores with El-Bahariya high-Mn iron ores, at 1:6 mixing ratio.

-Standard specifications of raw materials used for ferromanganese production, according to*the Indian Bureau of Mines (2014):*

- ► The maximum content of Fe must not exceed 15%, while the minimum content of Mn must be 38%.
- ► The proper Mn/Fe ratio for the ferromanganese alloys starts at 6.0.
- ► The sum of slag constitutes (Al_2O_3+SiO_2) must not increase more than 8% in the raw materials.
- ► The maximum content of phosphorous in the blended ores is recommended to be 0.16% P_2O_5, while the maximum concentration of sulfur is tolerant at 0.14% SO_3.

Chemical assays of the blend ratios.

Major oxides (100%)	Blend ratios (El-Gedida sample/ Um Bogma sample)				
	1/2	1/3	1/4	1/5	1/6
SiO_2	0.87	0.85	0.80	0.79	0.74
Al_2O_3	0.46	0.51	0.62	0.71	0.79
MnO	63.51	69.42	74.12	76.64	78.24
Fe_2O_3	25.17	20.20	16.18	14.85	13.05
MgO	0.21	0.26	0.29	0.34	0.38
CaO	1.94	1.54	1.39	1.22	0.96
Na_2O	1.35	0.99	0.86	0.76	0.62
K_2O	0.75	0.79	0.85	0.88	0.94
P_2O_5	0.09	0.08	0.07	0.06	0.06
SO_3	0.25	0.19	0.16	0.14	0.11
Cl	0.98	0.85	0.71	0.59	0.37
L.O.I	4.41	4.30	3.92	3.01	3.77

Concerns of El-Bahariya high-Mn iron ores

- The chemical analysis of El-Gedida high-Mn iron ore reveals that the total contents of iron and manganese are 46.37 wt. % Fe and 7.53 wt. % Mn.
- The maximum content of manganese in iron ores exploited for the steelmaking must not be more than 4 wt. % Mn.
- The high content of manganese in the studied iron ore will cause increasing the consumed quantity of coke during the reduction process and a detrimental effect on the productivity and life time of the blast furnace.
- Both physical and chemical properties of Fe-minerals are similar to that of Mn-minerals, making their separation from each other is difficult.

Ti-Minerals:

Ilmenite: $FeTiO_3$
Rutile: TiO_2

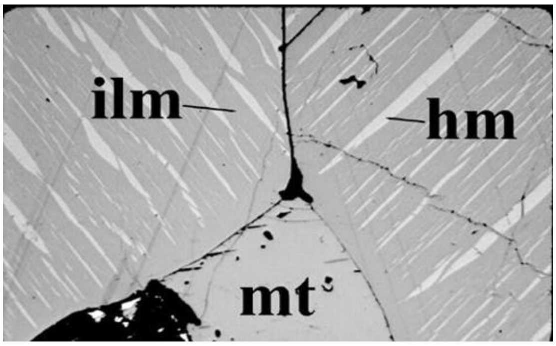
- **Origin:**

Ti-minerals are of magmatic segregation and weathering processes of the pre-existing rocks "alluvial placer". They occur as hard deposit (e.g. ilmenite deposits located in the Central Eastern Desert at several localities among which Hamra Dome, Abu Dahr, Wadi El-MiyahandAbu Ghalga) or loose black sand (e.g. rutile and ilmeniteon the Eastern Part of the Mediterranean part). The Ilmenite/black sands in Egypt are beach placers deposited by Nile stream during flooding seasons reaching the Mediterranean Sea at river mouth.

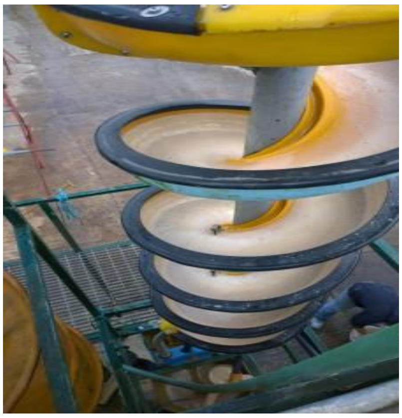
- **Pre-treatment & Beneficiation Processes:**

The hard deposit type is passed through a complex operational sequence: size reduction, sieving, and hydrometallurgy to reduce the unwanted iron content.

For example,the beneficiation process of Abu Ghalgailmenite is a complex and expensive operation. This is due to the complicated textural relationships between Ti and Fe minerals, exolution texture. Thus, there is no suitable physical operation for upgrading Abu Ghalga ore.The hydrometallurgical process of Abu Ghalgailmenite can be performed using HCl in order to remove iron mineral (17-28% Fe_2O_3) and recovery Ti minerals (36-49% TiO_2).The commercial Ti deposits contain 44-70% TiO_2.



On the other hand, Ti minerals present in sand deposits are liberated by nature, and the mining work can be done on *the low grade sands (5%ilmenite)* if the Ti mineral is of high quality.We can conclude that the separation and liberation of Ti minerals from sand deposits are easy and low cost compared to the hard type.The mineral processing technique used for ilmenite sand is a wet spiral separator.The wet spiral separator depends on the difference of size and density between the mineral particle of slurry.The lighter particles climb toward the outer rime of spiral trough while the heavier ones are concentrated in the center of spiral trough.



- **Industrial Applications:**

Titanium is a strong and light metal. It is as strong as steel and twice as strong as aluminum. Titanium is 45% lighter than steel and 65% heavier than aluminum.Due to its resistance to corrosion by seawater, titanium contributes to several parts of boats and ships such as propeller shafts and serves as coating of the oil transport pipes running under the seawater.

Titanium is characterized by a high strength, low weight and resistance to high temperature, therefore, it is used for manufacturing of airplanes and rockets.Titanium does not react within the human body so it is used to create artificial hips for setting bones.

Lecture#9: Industrial Minerals and their Usage-Barite, Glauconite, and Feldspar

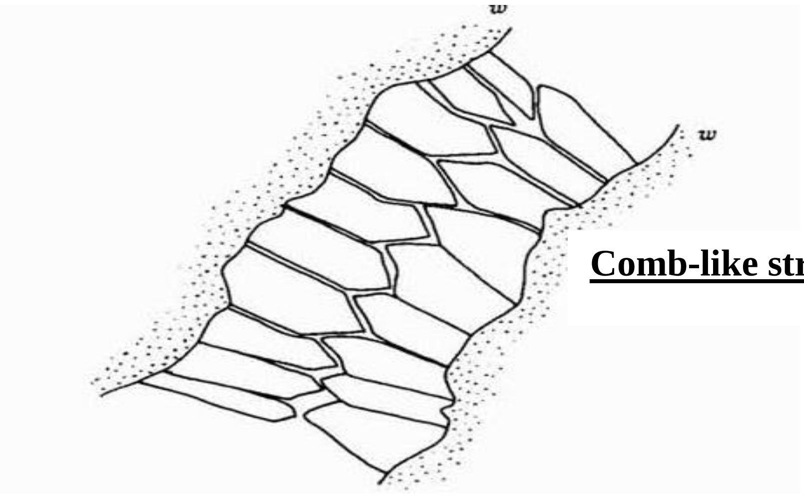
Barite:

Barite: $BaSO_4$

- **Origin:**

Barite can be precipitated directly from seawater or associated with the hydrothermal activities.

It occurs either in crystalline form, as tabular, prismatic, or bladed crystals, sometimes as a "comb" habit, or else massive. It is often colorless, cream-colored or white, but may also be yellow, blue, pink or brown.



Comb-like structure of barite

What is the comb-like structure???

The crystal growth increases inward from the wall as a comb-like shape. This structure type is common for minerals that tend to crystallize in elongate forms are arranged with their long axes (e.g. quartz & barite). This is compelling evidence on the direct precipitation in open-spaces from hydrothermal solutions.

- **Types of barite deposits**

Four types of barite deposits can be distinguished:

1-Bedded-sedimentary barite

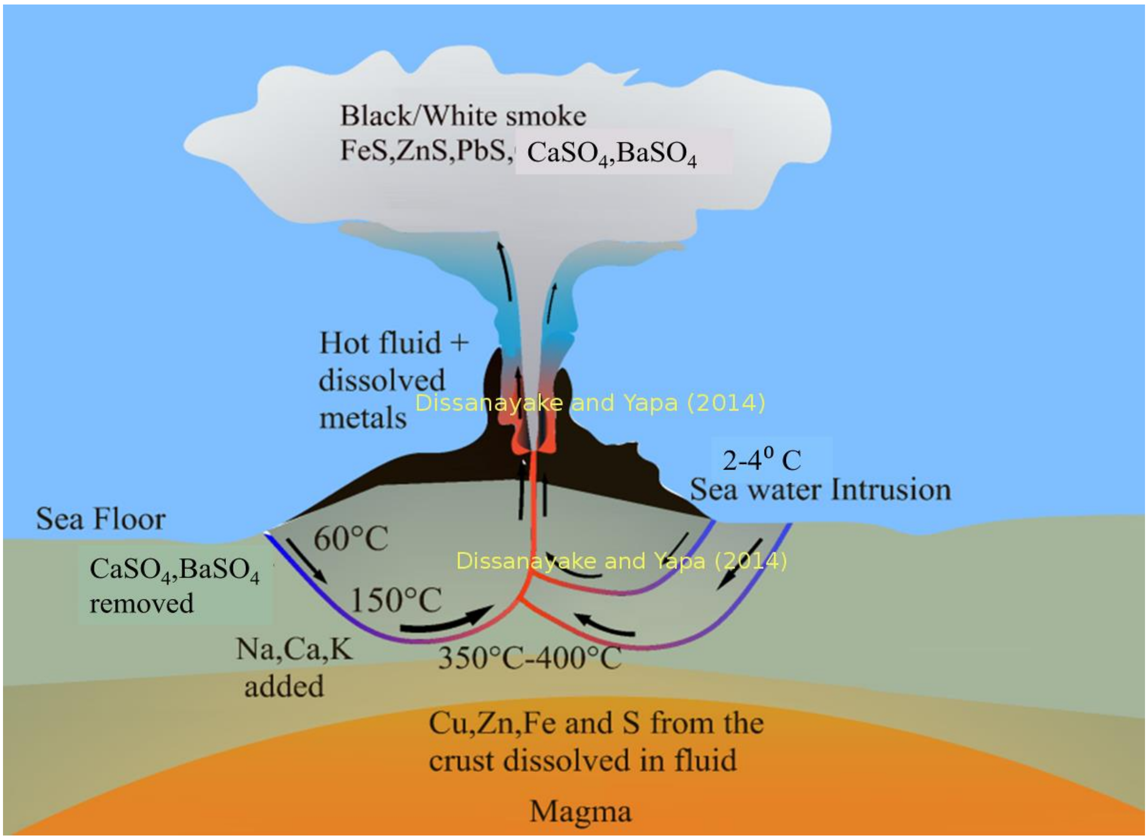
- Bedded-sedimentary deposits are stratiform bodies of massive or near-massive barite within sedimentary successions that typically contain organic-rich shale, mudstone, or chert.
- The barite can be dark in color, reflecting the presence of organic carbon.
- This deposit type has been attributed to an oceanographic process that operates beneath waters with high biological productivity. Decomposition of sinking organic matter promotes anoxic conditions by consuming dissolved oxygen, and it also releases organic-bound barium. The released barium combines with seawater sulfate to form barite, which accumulates on the sea floor at the interface between anoxic and oxic water masses.

2-Bedded-volcanic barite

- Bedded-volcanic deposits are stratiform bodies of massive or near-massive barite within stratigraphic successions containing igneous rocks—typically both felsic and mafic volcanic varieties—and sedimentary rocks.
- Bedded-volcanic barite deposits form at submarine volcanic centers at divergent, convergent, and, in some cases, transform plate boundaries. Barium

is scavenged from the volcanic edifice and underlying rocks by seawater that is heated by magmas and circulated by convection.

- Barite deposits form where the hot barium-bearing fluids are expelled onto the sea floor and encounter cold sulfate-bearing seawater.
- So, they can be intergrown or interbedded with copper, lead, zinc, or gold- or silver-bearing sulfide mineralsthat occur in the form of black/white smoker.



- **Pre-treatment & Beneficiation Processes:**

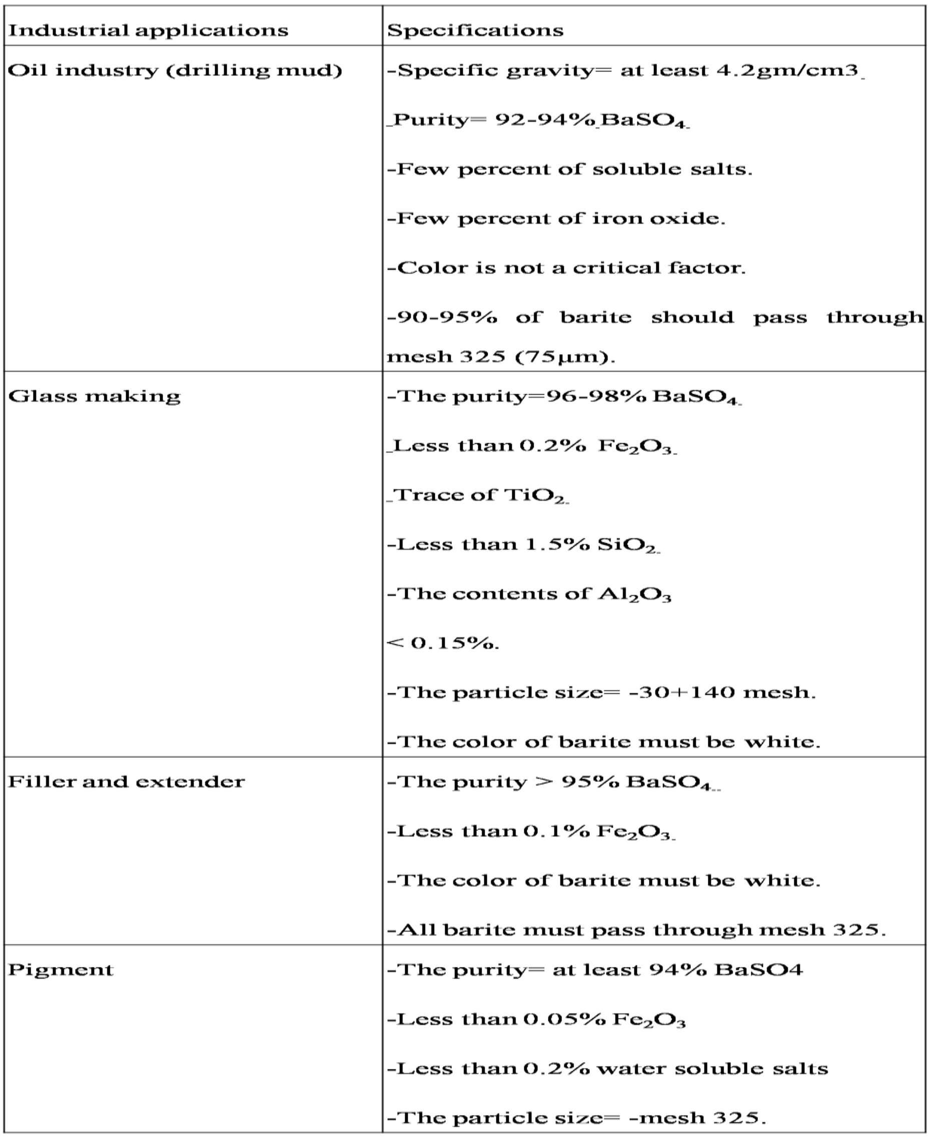
Barite deposits require size reduction to achieve the optimum size for a specific industrial application. Also, pre-treatment with HCl solution is needed for removal iron impurities.

- **Industrial Applications:**

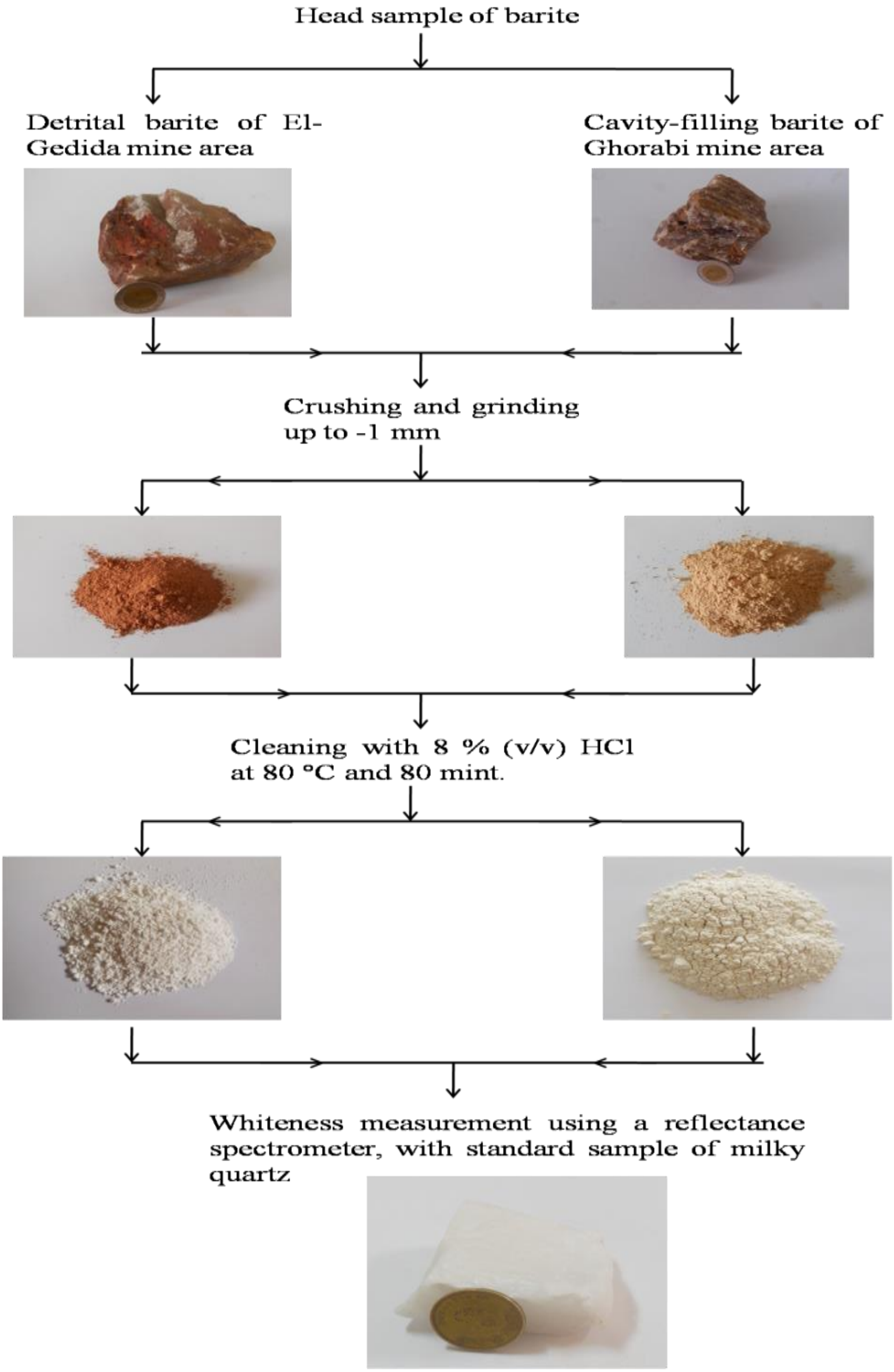
Barite is characterized by high specific gravity of 4.5 gm/cm^3. So, approximately 80% of the world's production of barite is widely and essentially used in the petroleum industry for making what is so-called drilling mud.

- There are three reasons regarding barite exploitation as a weighting agent during the process of drilling mud:

1. The first one <u>is the high specific gravity of such mineral</u>, resulting in increasing the density of the drilling liquid.
2. Barite is <u>a soft mineral; thereby it does not cause any damaging to drilling tools, and acts as a lubricant.</u>
3. <u>Barite is chemically inert material.</u>



Industrial applications	Specifications
Oil industry (drilling mud)	-Specific gravity= at least 4.2gm/cm3 -Purity= 92-94% $BaSO_4$ -Few percent of soluble salts. -Few percent of iron oxide. -Color is not a critical factor. -90-95% of barite should pass through mesh 325 (75µm).
Glass making	-The purity=96-98% $BaSO_4$ -Less than 0.2% Fe_2O_3 -Trace of TiO_2 -Less than 1.5% SiO_2 -The contents of Al_2O_3 < 0.15%. -The particle size= -30+140 mesh. -The color of barite must be white.
Filler and extender	-The purity > 95% $BaSO_4$ -Less than 0.1% Fe_2O_3 -The color of barite must be white. -All barite must pass through mesh 325.
Pigment	-The purity= at least 94% BaSO4 -Less than 0.05% Fe_2O_3 -Less than 0.2% water soluble salts -The particle size= -mesh 325.


Head sample of barite
Detrital barite of El-Gedida mine area
Cavity-filling barite of Ghorabi mine area
Crushing and grinding up to -1 mm
Cleaning with 8 % (v/v) HCl at 80 °C and 80 mint.
Whiteness measurement using a reflectance spectrometer, with standard sample of milky quartz

Glauconite:

Glauconite: $[(K, Na, Ca)(Fe^{+3}, Al, Mg)(Si, Al)O_{10} (OH)_2]$

- **Origin:**

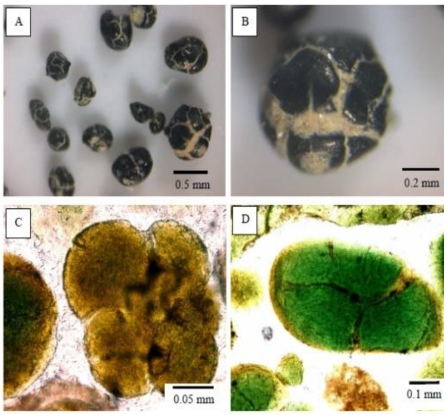
Glauconite refers to a green, iron and potassium-rich phyllosilicate with interstratified crystal structure of expandable and non expandable minerals. Glauconite consists of two end members of smectite (expandable) and mica (non expandable).Glauconite mineral is formed under shallow-deep marine conditions at depth ranging between 50-500m.

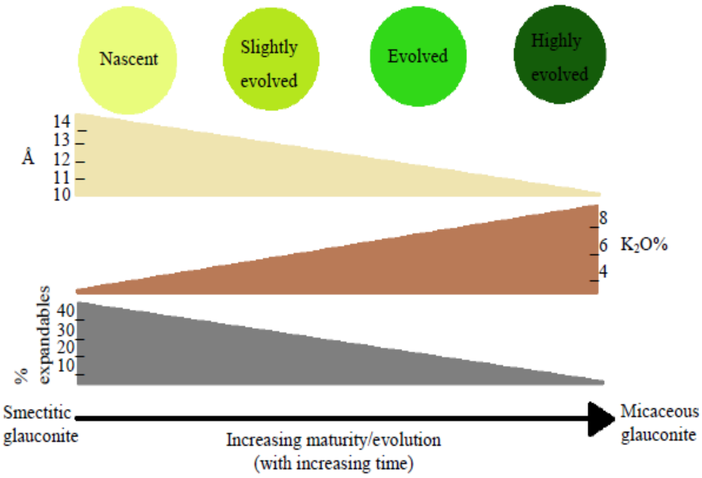
Two theories have been proposed for the interpretation of glauconite genesis:

1. **Layer lattice theory:**a degraded silicate lattice absorbs Fe and K from the ambient seawater.
2. **Neoformation theory:**evolution of the glauconite precursor (Fe-smectite) that was formed by the direct precipitation.

Depending on K content, glauconite can be evolutionarily classified into three types:

1. Nascent glauconite with low maturity (4% > K2O).
2. Slightly evolved glauconite with moderate maturity (4-6% K2O).
3. Evolved glauconite with high maturity (6-8% K2O).
4. High evolved glauconite with very high maturity (8% < K2O).





- **Pre-treatment & Beneficiation Processes:**

✓ *Size reduction and sieving up to a specific fraction where glauconite grains are concentrated.*

✓ *Sometimes, dry-high intensity magnetic separation is required in case of high impurities content (e.g. quartz, calcite, and gypsum).*

- **Industrial Applications:**

✓ Glauconite deposits are exploited as natural potassium fertilizers either in the **granular form** (*after size reduction, sieving, and magnetic separation*) or as **liquid fertilizer** (*after adequate thermal treatment in the presence of $CaCl_2$, which accelerates the release of K from glauconite crystal lattice at the contact with water*).

✓ Glauconite can also be used for water treatment (***as water softener***) *due to its ability to adsorb some heavy metals dissolved in water.*

Feldspar:

Orthoclase $KAlSi_3O_8$
Microcline $KAlSi_3O_8$
Albite $NaAlSi_3O_8$
Anorthite $CaAl_2Si_2O_8$

- **Origin:**

Feldspars are crystallized from magma and pegmatitic stage as solid solutions between Ca-, Na-, and K-feldspars:

Alkaline feldspar: This is feldspar with chemistry ranging between the potassium and sodium end members.

Plagioclase feldspar: This is feldspar with chemistry ranging between the sodium and calcium end members.

Potash spar: Potash spar is principally orthoclase or microcline and contains at least 10% K_2O.

Soda spar: Soda spar is mostly albite and contains at least 7% Na_2O.

Calcium spar: This is principally anorthite.

- **Pre-treatment & Beneficiation Processes:**

Most commercial feldspars are produced by flotation and magnetic separation followed by milling. Air classification is used for the finest grades.

- **Industrial Applications:**

Two major applications for feldspar worldwide are glass and ceramics:

Glassmaking:

Glass-grade products are typically coarsely ground, 20-40 mesh, and contain 4-6% K_2O, 5-7% Na_2O, about 19% Al_2O_3, and less than 0.1% Fe_2O_3. Feldspar is used mainly as a source of alumina, which improves both the workability of the glass melt and the chemical and physical stability of the finished product. It also provides the alkaline oxides (Na_2O, K_2O) that provide fluxing in partial substitution for calcium oxide, which improves chemical resistance, and for more expensive soda ash.

Ceramic industry:

Feldspars (*120-200 mesh*) are used for ceramic industry due to their effective role in improving the strength, toughness, and durability of the ceramic body.

Questions to be answered

-Barite is commonly used for oil industry, why???

-Glauconite is considered a good soil conditioner, why???

-Glauconite is considered a slow-release K fertilizer, why???

-Feldspar is used as fluxing agent for glassmaking industry, why???

Lecture#10: Application of Minerals in Some Chemical Reactions

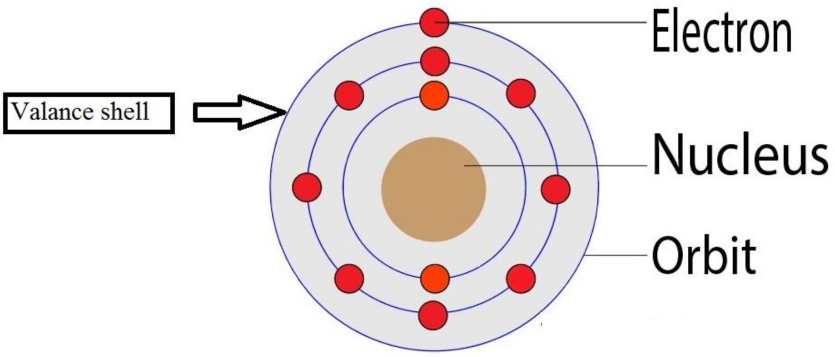
What is a catalyst in chemistry???

The term *catalyst* refers to any substance that accelerates the reaction rate without any consumption for this substance. Catalysts are divided into three main types: solid (e.g. hematite and pyrite for water splitting and hydrogen generation) liquid (e.g. enzymes that are lower the activation energy of the biochemical reactions inside cells, leading to fast the reaction rate), and gaseous types (e.g. oxides of nitrogen that serve as catalysts for the oxidation of sulfur dioxide during sulfuric acid production).

On the other hand, catalysis is classified as homogeneous (catalysts and reactants are all in the same physical state, for example, sulfuric acid in the production of diethyl ether from ethyl alcohol) and heterogeneous reactions (catalysts and reactants are in a different physical state, for example, hydrogenation of atmospheric nitrogen on the surface of iron particles during ammonia production).

Application of some minerals in the photo-electrochemical "PEC" cells

First of all, atoms consist of nuclei that are surrounded by specific number of electron-bearing orbits. The mostouter orbital contains valance electrons and called **the valance shell or valance band** (e.g. atom of Na metal).

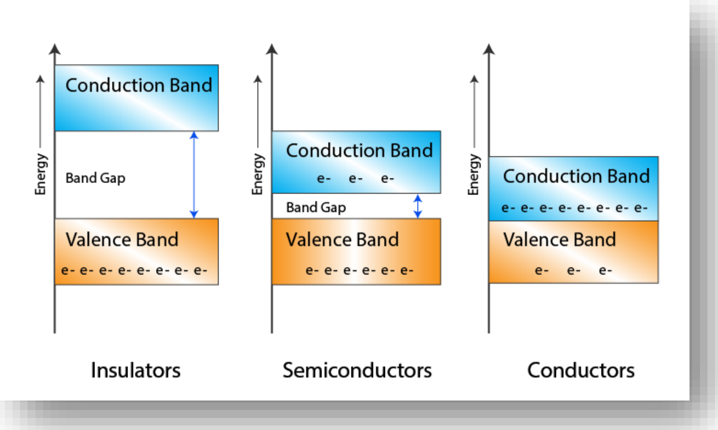


Sodium Electron Configuration

Another term you must know is what **so-called the conduction band**: a band contains freely moving electrons that migrated from the valance band up on exciting by external energy source. These excited electrons can create an electrical current as they move from anode side to cathode side.

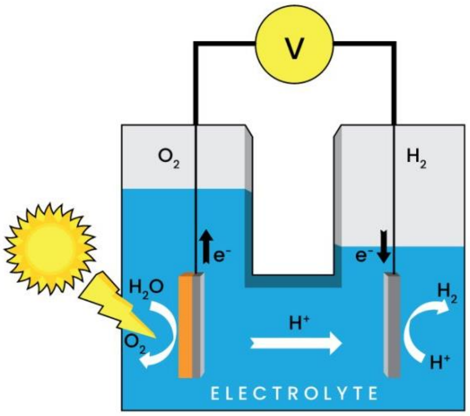
The distance between the valance band and conduction band **is known as the band gap**. Other definition, the difference in energy required to excite the valance electrons to migrate from the valance band to conduction band.

Depending on the band gap, the solid materials can be classified as conductors (e.g. metals), semi-conductors (e.g. Si and metal oxides), and insulators (e.g. silicate minerals like talc and asbestos).



How Does PEC work???

- The photo-electrochemical cells are promising devises for the generation of eco-friendly energy by water splitting into hydrogen and oxygen.
- Such cells are made up of one side engineered from photo-sensitive material (semi-conductor) (photo-anode) and another side represented by metal conductor (cathode).
- When light illuminate the anode, electrons on the valance band get excited to the conduction band, and leaves holes behind. These excited electrons become free electrons and follow through the external circuit to reach the cathode. At this site, protons (H^+) are reduced to H_2 gas, while the left holes on the photo-anode will oxidize water molecules into O_2.



Photoelectrochemical Cell

Minerals as photo-anodes

-Photo-anodes are made up of metal oxides like hematite (Fe2O3) and rutile (TiO2) due to several reasons among which:

-Their low cost.

-Low toxicity.

-Their electrochemical stability and corrosion resistance.

-Suitable band gap energy (1-4 eV) for an efficient absorption of the incident visible light. The larger band gap energy than 4 eV will require more energy to excite the electrons of valance band (e.g. UV and IR-lower wavelengths & higher frequencies). These wavelengths constitute a specific portion of the incident sunlight, while the visible wavelengths comprise the major portion.

Questions

Student name:…………………………………………..

Marks:

Determine the true and false statement of the following

1. The term mineral refers to an inorganic, solid, naturally occurring material characterized by unique chemical composition.

2. The metallic bond is largely responsible for some physical properties of minerals like malleability and tenacity.

3. The hydrothermal water of black smokers is mainly driven from the partial melting of peridotite rocks.

4. The melting point of sulphide minerals is higher than that of silicates.

5. Three origins can be presumed for iron minerals namely, sedimentary, hydrothermal, and magmatic.

6. The transformation of graphite into diamond can be done only by increasing the surrounding temperature conditions.

Complete the following statements with one/or maximum three words

1. If a rotational symmetry axis repeats a crystal face four times through the horizontal plane, the rotational angle will be**…………..**

2. The approximate difference in ionic radii for the mineral substitution reactions is**……………..**

3. When two minerals have the same crystal structure, this feature is called…….

4. Among minerals used for PEC cells are………… and…………

5. Both halite and calcite are crystallized by…………….. processes.

<u>Illistrate with drawing the following cases "6marks/point"</u>

1. Bowen's reaction series.
2. Rock cycle.
3. Beneficiation flowsheet of El-Bahariya barite deposits.
4. Flowsheet for fertilizer production from glauconite.
5. Moh's scale of mineral hardness.

<u>Give a suitable reasonfor the following cases "6marks/point"</u>

1. Feldspars cannot be exploited for Al metallurgy, why?
2. Most metallic minerals show little color variations, why?
3. Plutonic rocks are always characterized by phaneritic texture, why?
4. We can see plutonic rocks on the Earth's surface, why?
5. Ice cannot be considered as a mineral, why?

……

وصف المعادن اليدوية practical course

اسم المعدن	تركيبه الكيميائي	اللون	المخدش	البريق	الشفافيه	التشقق	الصلابه	المكسر	الاستخدام
1- الكوارتز	SiO_2	أبيض	أبيض	زجاجي	شفاف	لا يوجد	7	محاري conchoidal	احجار الزينه، الزجاج، السنفره
2- الكالسيت	$CaCO_3$	أبيض شفاف	ابيض	زجاجي	شفاف	3 مستويات	3	محاري conchoidal	صناعه الاسمنت، مواد البناء، احجار الزينه
3- البلاجيوكليز	$NaAlSiO_3$ $CaAl_2SiO_8$	أبيض	أبيض	زجاجي	غير شفاف	2مستويات	6.5 -6	غير مستوي uneven	صناعة السيراميك والزجاج، الخزف
4- الارثوكليز	$KAlSiO_8$	لحمي	أبيض	زجاجي	غير شفاف	2 مستويات	6	غير مستوي uneven	صناعه الخزف
5- التلك	$(OH)_2Mg_3Si_4O_{10}$	أخضر	أبيض	لؤلؤي صابوني	غير شفاف	1 مستوي	1	غير مستوي uneven	صناع بودره التلك، الصابون، البويات، الورق
6- الجبس	$CaSO_4.2H_2O$	أبيض	أبيض	زجاجي	شفاف	2 مستوي	2	محاري conchoidal	صناعة المصيص عجينه باريس في طب الاسنان
7- البيوتيت	$(OH)_2K(Mg,Fe)_3AlSi_3O_{10}$	أسود	أسود	حريري زجاجي لؤلؤي	شفاف	1 مستوي	3 -2.5	متورق micaceous	العوازل الكهربيه والحراريه
8- المسكوفيت	$(OH)_2KAl_3Si_3O_{10}$	فضي	أبيض	حريري زجاجي لؤلؤي	شفاف	1 مستوي	2.5 -2	متورق micaceous	المواد العازله
9- الكبريت	S	أصفر	أبيض مصفر	صمغي	شفاف الي شبه شفاف	لايوجد	2.5-1.5	كتلي massive	صناعه البارود والثقاب موصل ردئ للحراره
10- الجالينا	Pbs	رمادي الي رصاصي	رمادي الي رصاصي	فلزي	معتم	3 مستويات	3 -2.5	مستوي، محاري conchoidal	مصدر لفلز الرصاص وخام هام للفضه

Mahmoud Ali

اسم المعدن	تركيبه الكيميائي	اللون	المخدش	البريق	الشفافيه	التشقق	الصلابه	المكسر	الاستخدام
-11 الماجنيتيت	Fe_3O_4	أسود	أسود	فلزي	معتم	لايوجد	6 - 5	غير مستوي uneven	من الخامات الهامه للحديد، ذو مغناطيسيه عاليه
-12 الهيماتيت	Fe_2O_3	أحمرطوبي	أحمرطوبي	فلزي	معتم	لايوجد	6.5-5.5	غير مستوي uneven	صناعه الحديد والصلب والبويات
-13 الليمونيت	$2Fe_2O_3.3H_2O$	بني مصفر	أصفر	فلزي	معتم	لايوجد	5.5 -5	غيرمستوي uneven	يستخدم كخام للحديد وصناعة الاصباغ
-14 الكروميت	$Fe\ Cr_2\ O_4$	أسود	أسود	فلزي	معتم	لايوجد	5.5	محاري conchoidal	صناعه الصلب تغطية الفلزات صناعة البويات
-15 المينيت	$FeTiO_3$	أسود	أسود	فلزي	معتم	لايوجد	6-5	محاري conchoidal	مصدر لخام التيتانيوم ، صناعه البويات
-16 اسبستوس	$Mg_3\ Sio_5(OH)_4$	أبيض بني	أبيض	حريري	شبه شفاف-معتم	لايوجد	3-2.5	الياف	البناء ،العوازل اغلفه الابولب المقاومه للحر يق وكذلك الملابس اسمنت اسبستو
-17 ملاكيت	$CuCO_3.Cu(OH)_2$	أخضر	اخضر فاتح	قاتم الي ترابي	معتم	1	4-3.5	غيرمستوي uneven	الزينه،القليل منه كخام للنحاس
-18 انهيدريت	$CaSO_4$	أبيض	أبيض	زجاجي	شفاف	1	3.5	غيرمستوي uneven	البناء الطباشير
-19 الاباستر	$CaSO_4.2H_2O$	أبيض	أبيض	زجاجي	شفاف	لايوجد	2	غير مستوي uneven	احجار الزينة
-20 بيريت	FeS_2	بني مصفر فضي	بني مصفر	فلزي	معتم	لايوجد	6.5-6	محاري conchoidal	انتاج ثاني اكسيد الكبريت لصناعة الورق وحمض الكبريتيك

Mahmoud Ali

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-21 هاليت	NaCl	أبيض	أبيض	زجاجي	شبه شفاف	لايوجد	2.5-2	محاري conchoidal	حفظ الاطعمه الصناعات الكيميائيه كترسيب الصودا
-22 فلورايت	$\mathrm{CaF_2}$	أخضر	أبيض	زجاجي	شبه شفاف	لايوجد والبعض يوجد	4	غيرمستوي uneven	صناعة الصلب والمواد الكيميائيه والخزف
-23 اسفلرايت	ZnS	اصفر	ابيض او بني فاتح	صمغي	معتم	لا يوجد	4-3.5	محاري conchoidal	خام اولي للزنك يحتوي علي جرمانيوم كادميوم والانديوم
-24 طباشير	$\mathrm{CaCO_3}$	أبيض	أبيض	ترابي	معتم	لايوجد	1	غير مستوي uneven	اداة للكتابه
-25 كالكوبيريت	$\mathrm{CuFeS_2}$	نحاسي اصفر ذهبي	أسود مخضر	فلزي	معتم	لايوجد	4-3.5	محاري conchoidal	خام هام للنحاس
-26 باريت	$\mathrm{BaSO_4}$		أبيض	زجاجي	شفاف		3.5-3	محاري conchoidal ،شظوي	مصدر خام الباريوم
-27 بيرولوسايت	$\mathrm{MnO_2}$	أسود	اسود	فلزي	معتم	مستوي واحد	2 2.5-	غير مستوي uneven مسنن	مصدر هام للمنجنيز، صناعه الحديد والصلب