CRYSTALLOGRAPHY AND MINERALOGY

UNITS – 3, 4 & 5

6 Yr. Int. **M.Tech.** Geological Technology & Geoinformatics
(Paper Code: MTIGT0306)

Georgius Agricola, 'Father of Mineralogy'
German scientist '**Georg Bauer**' - named by birth
First book on Mineralogy was written by him entitled :
'Bermannus, sive de re metallica dialogus '(1530)
A description of the ore mountain(Ergebrge) – Silver mining district.

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René Just Haüy (1743 –1822)
"Father of Modern Crystallography"
French (Paris) Mineralogist
generally known as **Abbé Haüy**

Syllabus

- 1. **Elements of Crystallography**: Crystalline and Amorphous forms - Symmetry and Classification of Crystals - System of Crystal Notation - (Weiss and Millerian) - Forms and Habits. Crystal Systems (Isometric, Tetragonal, Hexagonal, Orthorhombic, Monoclinic, Triclinic, Twinning - Crystalline Aggregates – Columnar, Fibrous, Lamellar, Granular - Imitative shapes and Psudomorphism. **12 Hrs.**

- 2. **Crystal Properties:** Space Symmetry Elements- Translation – Rotation- Reflection - Inversion Screw and Glide-point groups and Crystal classes - Derivation of 32 Crystal classes based on Schoenflies notation - Bravais lattices and their Derivation - An outline of Space Groups. X-ray Crystallography. **12 Hrs.**

- 3. **Physical Mineralogy**: Physical Properties: (Colour – Structure – Form – Luster - Transparency – Streak – Hardness – Specific Gravity – Tenacity – Feel – Taste – Odour) - Electrical, Magnetic and Thermal properties- Determination of Specific Gravity (Jolly's spring balance, Walker's steel yard, Pycnometer methods) - Empirical and Structural formula of minerals – Isomorphism, Polymorphism and Psudomorphism - Atomic substitution and Solid solution in minerals - Non Crystalline minerals - Fluorescence in minerals - Metamict state. **16 Hrs.**

- 4. **Optical Mineralogy:** Optical Properties (Colour – Form – Cleavage - Refractive Index - Relief – Alteration – Inclusions – Zoning – Pleochroism – Extinction - Polarization colours – Birefringence) – Twinning - Optic sign (Uniaxial and biaxial)- Interference figures - Primary and Secondary Optic axes - Optic axial angle measurements – Optic Orientation – Dispersion in Crystals - Optic anomalies. **12 Hrs.**

- 5. **Mineral Groups:** Ortho and Ring Silicates (Olivine group - Garnet group). Alumino silicates (Epidote group - Zirc[illegible]on – Staurolit[illegible] Beryl - Cordierite and Tourmaline). Sheet Silicates (M[illegible]up - Chl[illegible]ite grou[illegible] mi[illegible]als) - Cha[illegible]ates [illegible]up - [illegible]e gr[illegible] Wolla[illegible] Frame[illegible] Sili[illegible] - F[illegible]ar - Fe[illegible] - Z[illegible]pol[illegible]) - [illegible] (S[illegible] C[illegible] a[illegible] [illegible]tes).

PHYSICAL PROPERTIES OF MINERALS

LIGHT BASED CHARACTERS:

- **Colour**
  - **Streak** – colour of the mineral powder seen by scratching it over a porcelain rough surfaced plate.
  - **Play of colours-** displaying different colours from the reflected / refracted light.
  - **Change of colour** – changes the colour while viewing in different angles.
  - **Opalescence** – pearly / milky shining appearance
  - **Tarnish** – dull colour due to oxidation or chemical action of sulphur.
  - **Iridescence** – display of prismatic colours-interference of rays of light in minute fissures
- **Lustre** – Appearance of mineral in reflected light-Based on the intensity and kind depending upon the amount and type of reflection of light take place at their surfaces. Metallic, Sub metallic, Non-metallic, i.e., Glassy or Vitreous, Sub-vitreous, Greasy, Waxy, Resinous, Pearly, Silky, Adamantine or Brilliant and dull or earthy.
- **Transparency** – Transparent, Semi-transparent, Transluscent and Opaque.
- **Phosphorescence & Fluorescence** – Emitting light after having been subjected to heating, rubbing, electric radiation or to ultra-violet light. E.g. Diamond, Ruby-after exposed to X-rays. Fluorspar, Quartz-on rubbing together or while exposed to UV or other radiations in dark room.

SENSE BASED CHARACTERS:

- **Taste** – Water Soluble minerals - e.g.Saline- NaCl, Alkaline-Potash and Soda, Cooling – Nitre or Pottassium chlorate, Astringent – Green vitriol, Sweetish astringent- Alum, Bitter-Epsom, Sour-Sulphuric acid.
- **Odour** – When struck, rubbed, breathed upon or heated – e.g. Alliaceous-Garlic - Arsenic mnls; Horse radish – Selenium mnls; Sulphurous-rotten eggs-Pyrites, sulphides; Foetid-rotten eggs-Qtz, Lst.; Argillaceous-clayey- Shale.
- **Feel** – Smooth, Greasy, Unctuous, harsh / Meagre / rough. Certain mnls. Adhere to the tongue.

Hardness – Mohs' Scale of Hardness

1. Talc - $Mg_3Si_4O_{10}(OH)_2$
2. Gypsum - $CaSO_4 \cdot 2H_2O$
3. Calcite - $CaCO_3$
4. Fluorite - CaF_2
5. Apatite - $Ca_5(PO_4)_3(OH,Cl,F)$
6. Orthoclase - $KAlSi_3O_8$
7. Quartz - SiO_2
8. Topaz - $Al_2SiO_4(OH,F)_2$
9. Corundum - Al_2O_3

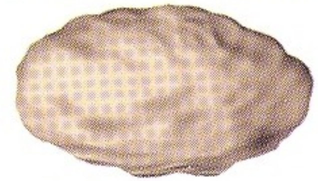
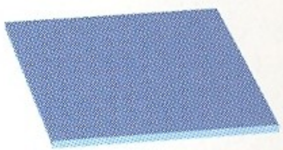
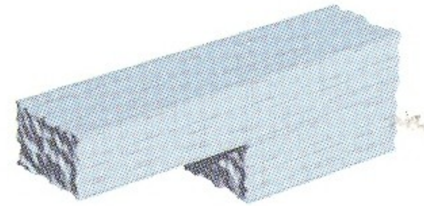
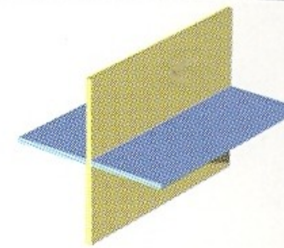
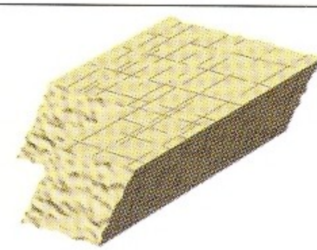
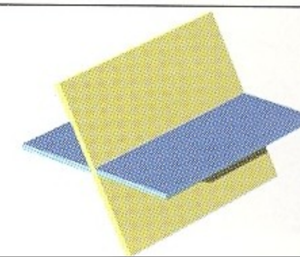
Tenacity

- **Sectility** – can be cut with a knife and breaksup under a hammer – Graphite, Steatite, Gypsum.
- **Malleability** – can be flattened under a hammer – Native Gold, Silver and Copper
- **Flexibility** – Remains bent after the removal of pressure – Talc, Selenite.
- **Elasticity** – bent portions will spring back to its former position - Mica, Chlorite.
- **Brittleness** – Crumbling or flying to powder – Iron Pyrites, Apatite and Flourspar.

Cleavage or Parting

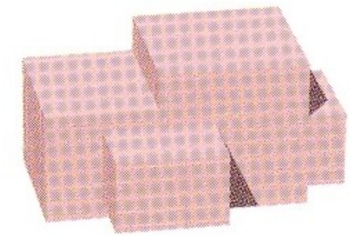
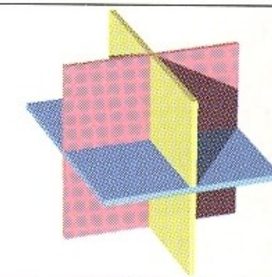
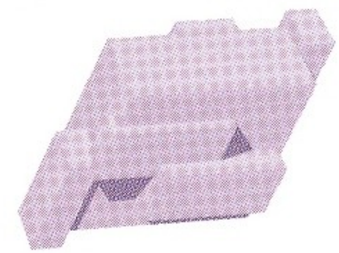
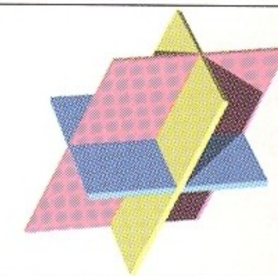
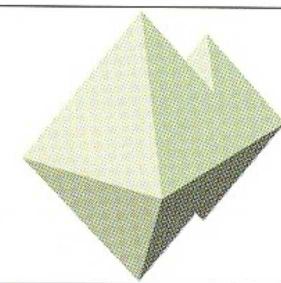
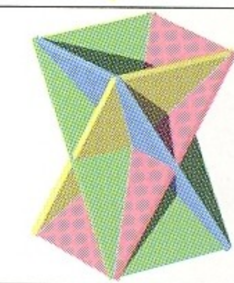
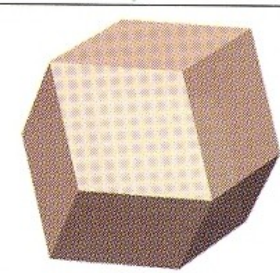
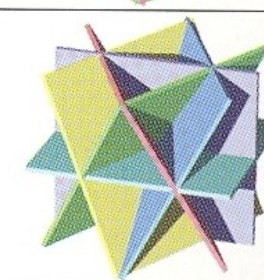
- The tendency of minerals to split along certain definite planes
- Cleavage is closely related to the crystalline forms and internal structure of the crystal
- The directions of the cleavage planes are parallel to a certain face or to certain faces of a form in which the mineral may crystallize
- In the plane of cleavage, the atoms of the mineral are more closely packed together or the mutual electrical charges are greater than in directions at right angles to the cleavage plane – plane of least cohesion
- Thus, it is Easy to split along cleavage plane
  - **Perfect** / Eminent - Parallel to base – **Basal** (Graphite, Mica)
  - **Cubic** (Galena), **Octahedral** (Flourspar), **Dodecahedral** (Garnet), **Rhombohedral** (Calclite), **Prismatic** ( ), **Pinacoidal** ( )
  - **Imperfect** (Feldspar), **Absent** (amorphous substances and Quartz).

3D images of mineral forms depicting Cleavages

Number of Cleavage Directions	Shapes that Crystal Breaks Into	Sketch	Illustration of Cleavage Directions
0 No cleavage, only fracture	Irregular masses with no flat surfaces		None
1	Basal cleavage "Books" that split apart along flat sheets		
2 at 90°	Elongated form with rectangular cross sections (prisms) and parts of such forms		
2 not at 90°	Elongated form with parallelogram cross sections (prisms) and parts of such forms		

3D images of mineral forms depicting Cleavages

…contd…

3 at 90°	Cubic cleavage Shapes made of cubes and parts of cubes		
3 not at 90°	Rhombohedral cleavage Shapes made of rhombohedrons and parts of rhombohedrons		
4	Octahedral cleavage Shapes made of octahedrons and parts of octahedrons		
6	Shapes made of dodecahedrons and parts of dodecahedrons		

Fracture

- Character displayed on the broken or chipped surfaces of minerals.
- Not connected with the crystalline structure of the mineral,
- Therefore, fracture of mineral has got no relation with cleavage
- So, Fracture has got irregular broken surface.
  - **Concoidal** – Curved concave or convex fractures on breaking – Quartz, Flint or natural glasses.
  - **Even** – Flat to nearly flat Fracture surface – Chert
  - **Uneven** – Rough fracture surfaces (Feldspars)
  - **Hackly** – studded with sharp and jagged elevations – as in broken cast iron (Asbestos)
  - **Earthy** – fracture of chalk, Meerschaum (Magnesite)

Surface Tension Effects:

The difference in adhesive power of various liquids to different minerals-useful for economic ore separation and concentration from its gangue.

SPECIFIC GRAVITY

- The ratio of the weight of the body to that of an equal volume of water.
- Basic idea: The loss in weight of a mineral immersed in water is the weight of volume of water equal to that of the mineral.

$$\frac{W_a}{W_a - W_w}$$

SPECIFIC GRAVITY

The specific gravity of a body is the ratio of the weight of the body to that of an equal volume of water.

Methods of determining Specific Gravity of Minerals:

Any of the following 6 methods can be chosen depending upon the size and character of the mineral specimen:

1. **Chemical Balance** – weight in air & weight in water can be measured and using the formula:

$$\frac{Wa}{Wa-Ww}$$

2. **Walker's Steel Yard** – Long graduated beam, pivoted near one end horizontally and counterbalanced by a heavy weight suspended to the short arm (Fig.)

$$\frac{b}{b-a}$$

3. **Jolly's Spring Balance –** Long vertically hanging spring with a graduated scale, attached with two scale-pans in the lower end of the spring, one below the other (Fig.)

$$\frac{b-a}{b-c}$$

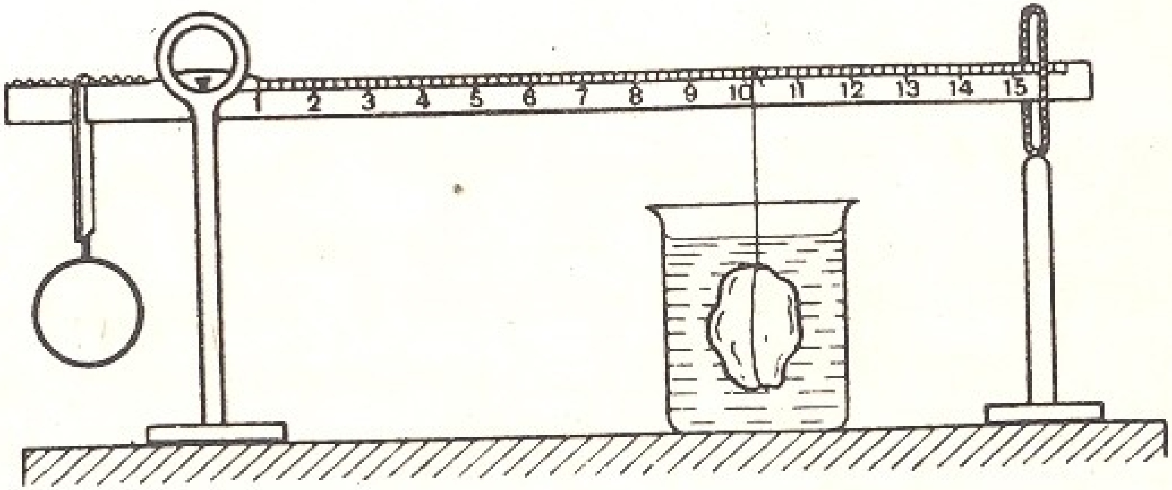


FIG. 15. Walker's Steelyard

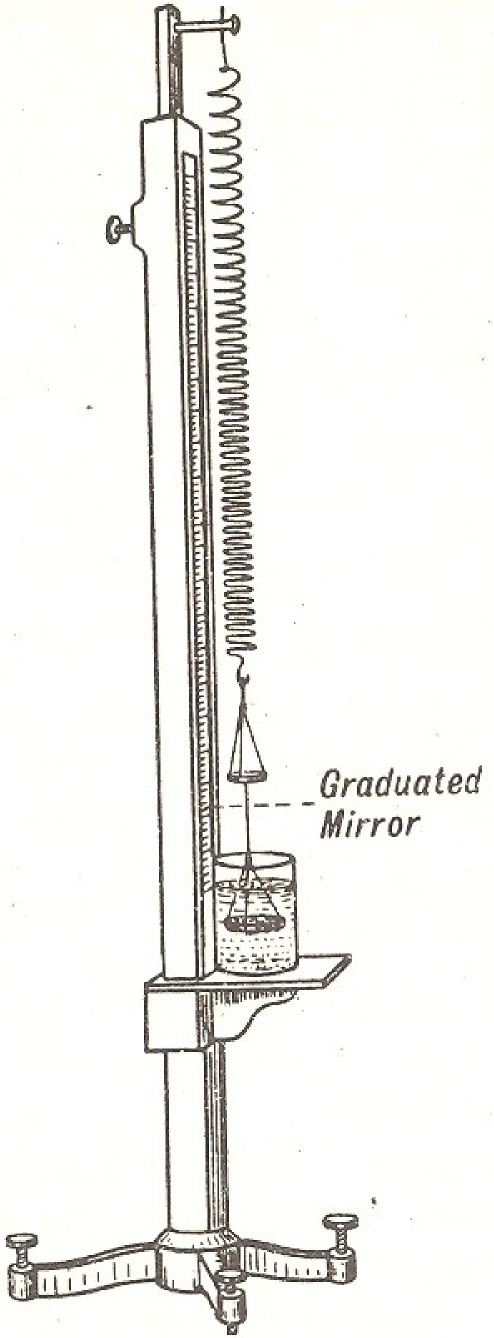
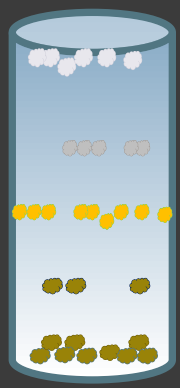
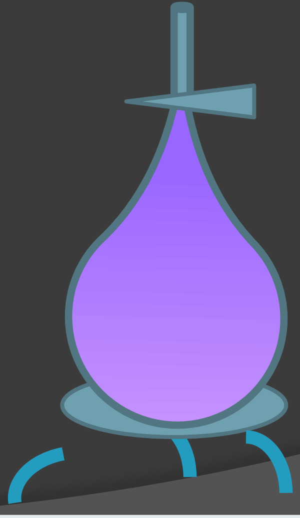


FIG. 16. Jolly's Spring Balance.

Heavy Liquids



Pycnometer
- Specific Gravity bottle
-Use distilled water



Methods of determining Specific Gravity of Minerals: ... contd…

4. **Increased Volume of Water while immersing minerals:** Rapid determination of large no. of uniform minerals can be determined through this method. Wt. in grams of mnl. in air divided by the increase in volume in cubic centimeters gives the approximate Sp.Gr. of mineral.

$$\frac{Wa}{Vi}$$

5. **Pycnometer / Specific Gravity Bottle :** Small fragments.

6. **Heavy Liquids for a mixture of minerals:** Heavy liquids of known specific gravity are used to determine relative specific gravity of minerals when they are available as a mixture of small grains.

MAGNETISM, ELECTRICITY & RADIOACTIVITY

- Magnetism
  - Highly Magnetic – Magnetite, Pyrrhotite
  - Moderately Magnetic – Siderite, Chromite, Ilmenite, Haematite, Wolframite
  - Non-magnetic – Quartz, Calcite, Feldspar, Corundum, Cassiterite.
- Electricity
  - Good conductors – Native metals, Sulphides.
  - Bad Conductors – Silicates
  - Pyroelectric mnls – On heating - Tourmaline
  - Piezoelectric mnls – Under Pressure - Quartz
- Radioactivity
  - Radioactive – Uraninite, Thorianite & Non-radioactive

HEAT BASED CHARACTERS:

- The relative fusibility of certain minerals is a useful character using blowpipe.
- Von Kobell's scale of Mineral Fusibility:
  - The following 6 minerals have the character of increase in **temperature of fusion** constantly.

Stibnite → Natrolite → Almandine → Garnet → Actinolite → Orthoclase → Bronzite.

Isomorphism, Polymorphism and Psudomorphism

- **Isomorphs:** Minerals with different chemical compositions; same crystal structure (belong to same crystal class)

- **Polymorphs:** Minerals with same chemical composition; different crystal structures

Isomorphism (Isostructuralism)

- Minerals with analogous formulas where the relative sizes of cations and anions are similar and crystal structure is identical or closely related
  - Typically (but not always) the basis for grouping and classification, e.g.
    - Garnet group, Amphibole group, Mica group, Pyroxene group

Galena, PbS

Halite, NaCl

Pseudomorphism and Polymorphism

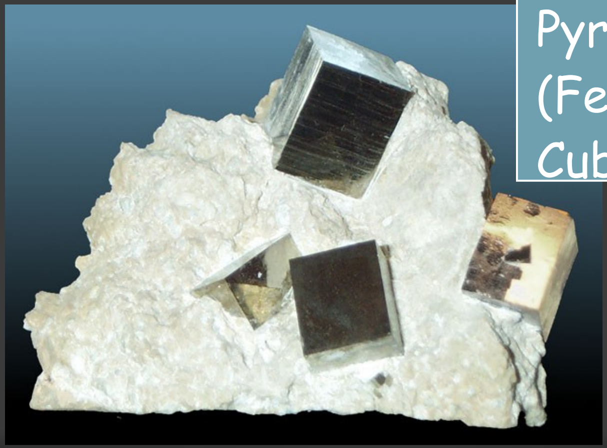
Pseudomorph of goethite after pyrite

- **Pseudomorphism** – the assumption by a mineral of a form other than that which really belongs to it, by incrustation, infiltration, replacement or by alteration.

- **Polymorphism** – Two minerals of markedly different physical properties, but may have identical chemical compositions.
  - **Dimorphism** - $CaCO_3$: Calcite – Aragonite,
    Carbon (C) : Graphite – Diamond.
  - **Trimorphous** – Titanium Dioxide (TiO_2) : Anatase-Brookite-Rutile.

Polymorphism

- The same chemical formula applies to two (or more) distinct mineral species
  - Chemical composition may not be sufficient to designate a specific mineral species (physically homogeneous and separable portion of a material system)
  - Polymorphs have different crystal forms (atomic arrangements) and different physical properties
  - Different polymorphs occur as a result of differing environmental conditions, principally temperature and pressure

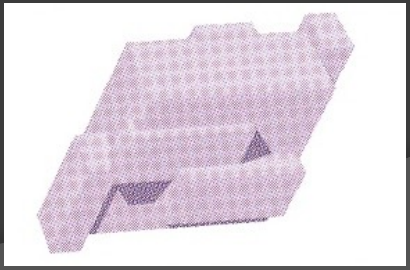


Pyrite, FeS_2 ($Fe^{+2}S_2$), Cubic

Marcasite, FeS_2 ($Fe^{+2}S_2$), Orthorhombic

Mineral-to-mineral substitution is replacement of Aragonite twin crystals – Orthorhombic – repeated twin crystals show pseudo-hexagonal forms

Fe oxides replacing pyrite cubes – Pseudomorph of Pyrite

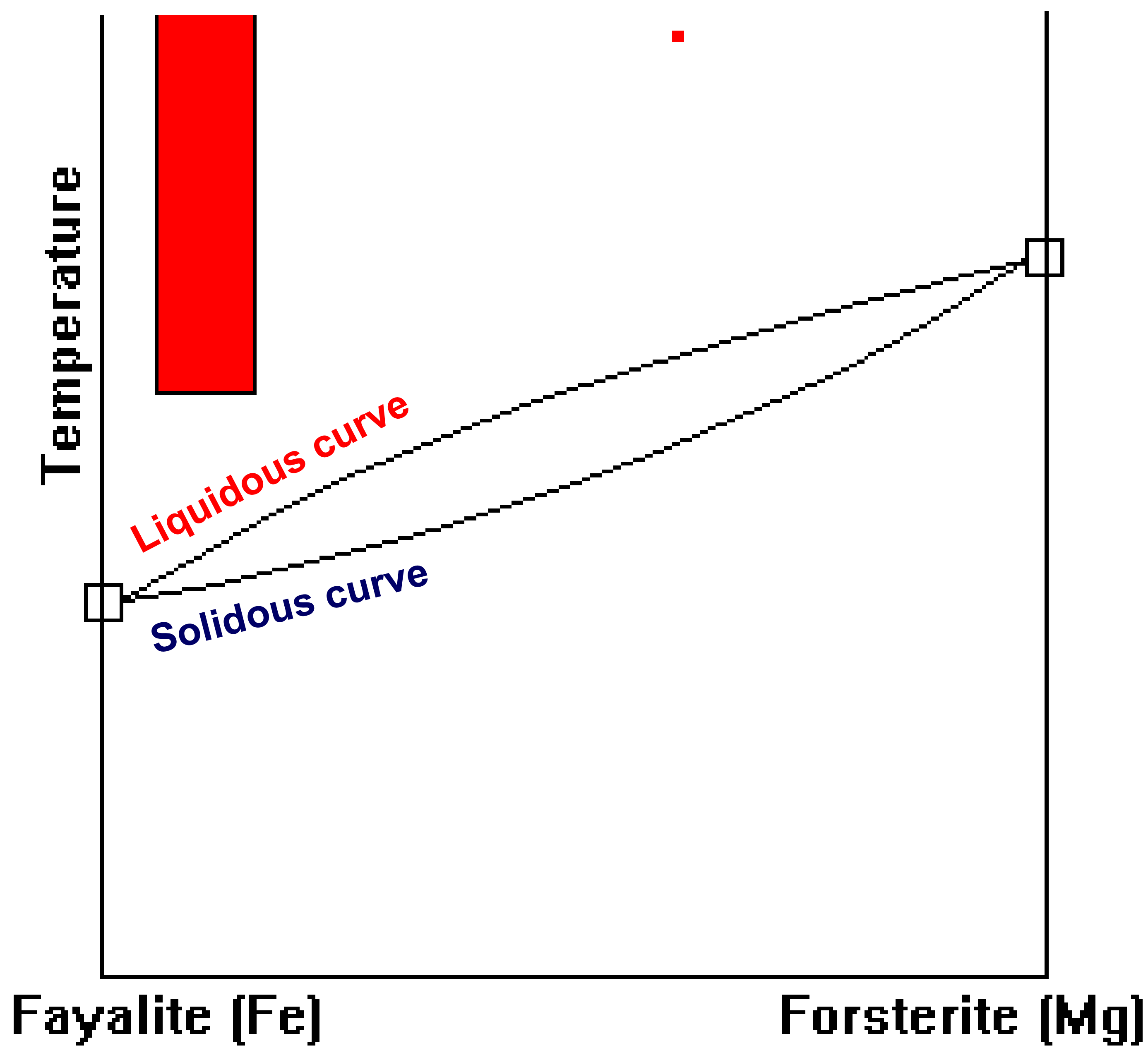


Calcite – Rhombohedral Division-Rhombohedral class

Atomic substitution & Solid solution in minerals

- When the chemical composition of a mineral varies because of atomic substitution, the mineral is said to exhibit "Solid Solution“. **Solid Solution** is defined as "a mineral structure in which specific atomic site(s) are occupied in variable proportions by two or more different elements." (Klein & Hurlbut, p.233)
- **Examples:** The **Olivine group** represents a complete solid solution series
- Compositions range from a 100% Mg-rich "end member" (Forsterite) to a 100% Fe-rich "end member" (Fayalite), with all mixtures of these two elements possible (e.g., 90% Mg and 10% Fe) complete solid solution series because Fe and Mg have same charge and similar ionic radius.

Majority of the rock forming silicates are isomorphous compounds. They are miscible in all proportions in solid state forming homogeneous crystals.


Temperature
Liquidous curve
Solidous curve
Fayalite (Fe)
Forsterite (Mg)

- Plagioclase Feldspars also display a complete solid solution series ranging from a 100% Na-rich end member (Albite) to a 100% Ca-rich end member (Anorthite), with all intermediate compositions possible.

- Because Na has a charge of +1 and Ca has a charge of +2, a double substitution must occur to maintain the charge balance. The other cations in the feldspar composition are Al (charge = +3) and Si (charge = +4). (Al and Si are close enough in size for substitution to occur)For each substitution of Ca (+2) for Na (+1), an equal amount of Al (+3) is substituted for Si (+4)

- e.g., a 50/50 mixture would have the composition:
- $Ca_{0.5}Na_{0.5}Al_{1.5}Si_{2.5}O_8$
- charge balance: (+2 x 0.5) + (+1 x 0.5) + (+3 x 1.5) + (+4 x 2.5) = +16
- which is balanced by -16 from oxygen

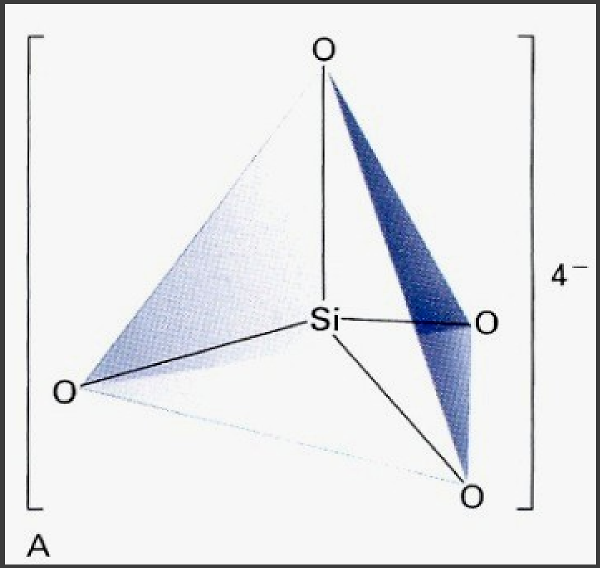
- In contrast Alkali Feldspars display only a limited solid solution series because the radius of K (1.33 Å) is significantly larger than that of Na (0.97 Å)

Solid solution in minerals...contd...

- Other than the Plagioclase Feldspars (Albite – Anorthite series), the Pyroxenes (Aegirine – Augite series), Amphiboles (Actinolite – Tremolite series) and Garnets (PYRALSPITE – Pyrope, Almandine, Spessartite and UGRANDITE – Uvarovite, Grossular, Andradite) are good examples of this type.
- The formation of such minerals from magmas follows totally different steps/patterns/lines to those followed by minerals of constant composition.

Empirical and Structural formula of minerals

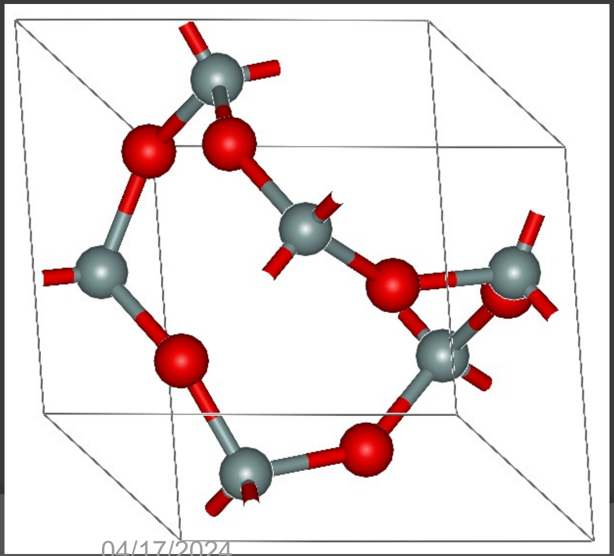
- The simplest types of chemical formulas are called ***empirical formulas***, which use only letters and numbers indicating atomic proportional ratios (the numerical proportions of atoms of one type to those of other types).
- The ***structural formula*** of a chemical compound is a graphic representation of the molecular structure, showing how the atoms are arranged. The chemical bonding within the molecule is also shown, either explicitly or implicitly.



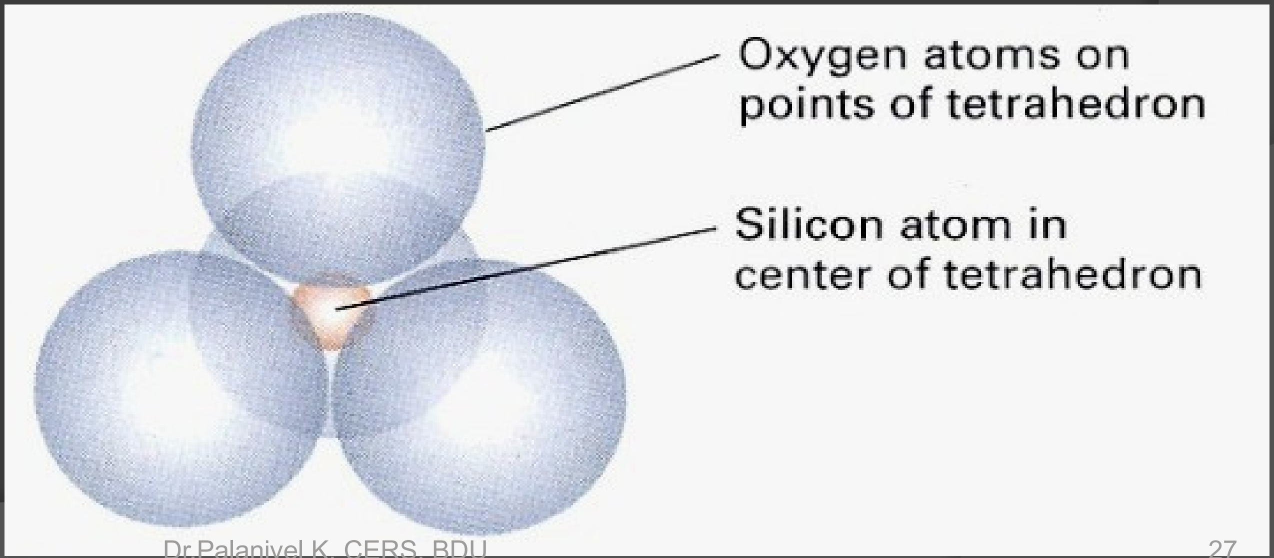
Silicate Tetrahedron – Fundamental building block of all silicate minerals – 3D Schematic representation / Structural formula of Quartz

Quartz is a mineral composed of silicon and oxygen atoms in a continuous framework of SiO_4 silicon–oxygen tetrahedra, with each oxygen being shared between two tetrahedra, giving an overall chemical / empirical formula of SiO_2.

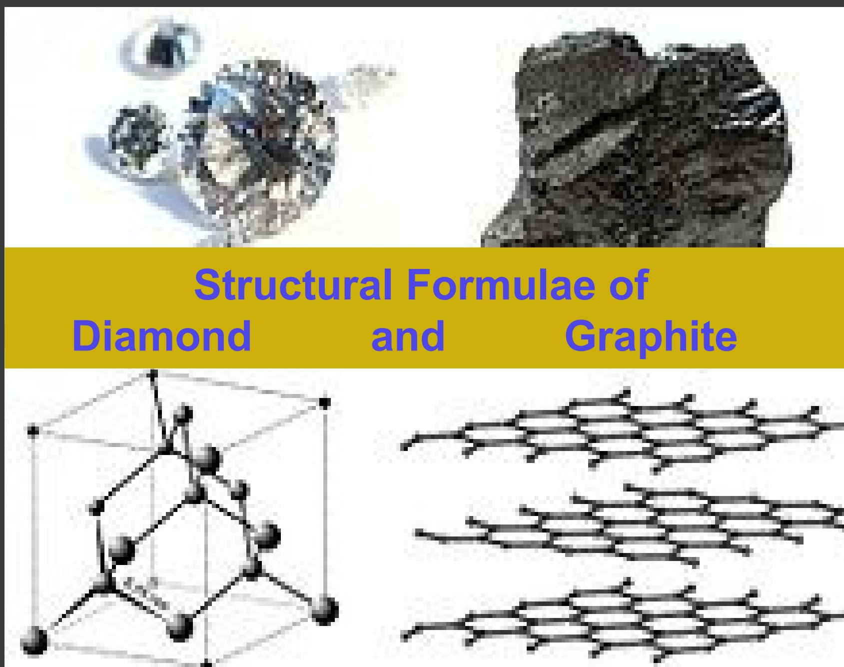
Crystal structure of α-quartz (red balls are oxygen, grey are silicon)



Proportionally accurate model

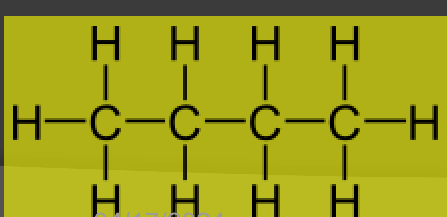


- Unlike **chemical** formulae or chemical **names**, **structural** formulae provide a representation of the molecular structures.



Empirical Formula of Diamond is C

X-ray crystallography revealed the arrangement of their atoms and thus the structural formula (bottom), which accounts for their different properties. In Diamond, the carbon atoms are arranged tetrahedrally and held together by single covalent bonds, making it strong in all directions. By contrast, Graphite is composed of stacked sheets. Within the sheet, the bonding is covalent and has hexagonal symmetry, but there are no covalent bonds between the sheets, making graphite easy to cleave into flakes.



Structural formula for butane. This is not a chemical formula. Examples of chemical formulas for butane are the empirical formula C2H5, the molecular formula C4H10, and the condensed (or semi-structural) formula $CH_3CH_2CH_2CH_3$.

Empirical and Structural formula of minerals

- The empirical formula is derived from the mineral's structural (molecular) formula by using the published analysis of the mineral or deriving the analysis using basic rules.
- Atomic substitutions were analyzed by the following procedure if published analyses were not available. Adjustments were made to match the measured density with the calculated density if needed:
- $(K,Na) = K_{0.75} Na_{0.25}$
- $(K,Na,Cs)= K_{0.6} Na_{0.3} Cs_{0.1}$

Empirical and Structural formula of minerals ...contd...

- In chemistry, the **empirical formula** of a chemical compound is the simplest whole number ratio of atoms of each element present in a compound.
- An empirical formula makes no reference to isomerism, structure, or absolute number of atoms.
- The empirical formula is used as standard for most ionic compounds, such as $CaCl_2$, and for macromolecules, such as SiO_2.
- The term **empirical** refers to the process of elemental analysis, a technique of analytical chemistry used to determine the relative amounts of each element in a chemical compound.
- In contrast, the molecular formula identifies the number of each type of atom in a molecule, and the structural formula also shows the structure of the molecule.
- For example, the chemical compound n-hexane has the structural formula $CH_3CH_2CH_2CH_2CH_2CH_3$, which shows that it has 6 carbon atoms arranged in a straight chain, and 14 hydrogen atoms.

- Hexane's molecular formula is C_6H_{14}, and its empirical formula is C_3H_7, showing a C:H ratio of 3:7.
- Different compounds can have the same empirical formula. For example, Formaldehyde, Acetic acid and Glucose have the same empirical formula, CH_2O. This is the actual chemical formula for Formaldehyde, but Acetic acid has double the number of atoms and Glucose has six times the number of atoms.
- The Rare Earth Elements (**REE in formulae**) were calculated based on the normalized abundances in **Chondrite** (meteorite).
- The Solid solution series minerals were calculated based on the mid-points of the accepted compositional range of the mineral.
- The empirical formula was used to calculate the chemical composition.

- While finding-out elemental composition of minerals and its chemical analysis, the chemical formula of minerals were attained.

- The structural formulas of many of the minerals have been erected with the help of **X-ray research techniques.** In many cases it was possible to spot mutual relations of atoms in crystalline structures of minerals.

- The Formulas of Minerals can be **empirical**, showing only an elemental composition, and **structural**, giving representation about a spatial arrangement of atoms in a mineral and their communication among themselves.

- In minerals, it is important to reveal cations and the anionic complexes characterizing types of crystalline structures. While writing formulas of minerals, anionic complexes [-ve] are separated by square brackets from cations +ve, for example, Siderite **Fe [CO_3].**
- It is necessary to mean, that empirical formulas of minerals do not map features of their interior structure and in mineralogy they are exchanged now by structural formulas. So, the **empirical formula** of a mineral of Muscovite **$H_2KAl_3Si_3O_{12}$**, and **structural formula** is :

  $KAl_2\ [AlSi_3O_{10}]\ (OH, F)\ _2$.
- Last shows that in Muscovite structure, there is the difficult anionic complex and that water in a Muscovite is not in view as H_2O, and in the form of hydroxyl (OH) - and this hydroxyl can in turn be replaced with F-.

Non-Crystalline minerals / Mineraloid

- A non-crystalline or mineraloid is a mineral-like substance that does not demonstrate crystallinity. Mineraloids possess chemical compositions that vary beyond the generally accepted ranges for specific minerals.
- For example, **Obsidian** is an amorphous glass and not a crystal. **Jet** is derived from decaying wood under extreme pressure.
- **Opal** is an another mineraloid because of its non-crystalline nature. **Pearl**, considered by some to be a mineral because of the presence of calcium carbonate crystals within its structure, would be better considered as a mineraloid because the crystals are bonded by an organic material, and there is no definite proportion of the components.

Metamict state

- **Metamictization** (sometimes called **metamiction**) is a natural process resulting in the gradual and ultimately complete destruction of a mineral's crystal structure, leaving the mineral amorphous. Affected material is therefore described as **metamict.**

- Certain minerals occasionally contain **interstitial impurities of radioactive compounds** and it is the alpha radiation emitted from these compounds that is responsible for degrading a mineral's crystal structure through internal bombardment.

- Effects of metamictization are extensive: other than negating any birefringence previously present, the process also lowers a mineral's refractive index, hardness, and specific gravity. The mineral's colour is also affected: metamict specimens are usually green or brown. Further, metamictization diffuses the bands of a mineral's absorption spectrum. Curiously and inexplicably, the one attribute which metamictization does not alter is **dispersion**. All metamict materials are themselves radioactive, some dangerously so.
- An example of a metamict mineral is **Zircon**. The presence of uranium and thorium atoms substituting for zirconium in the crystal structure is responsible for the radiation damage in this case. Unaffected specimens are termed as **high zircon** while metamict specimens are termed as **low zircon**. Specimens falling between the two extremes are termed **intermediate**.

- Other minerals known to undergo metamictization include **Allanite, Ekanite** and **Titanite**. Ekanite is almost invariably found completely metamict as thorium and uranium are part of its essential chemical composition.
- Metamict minerals can have their crystallinity and properties restored through **prolonged annealing**.
- A related phenomenon is the formation of **pleochroic halos** surrounding minute Zircon inclusions within a crystal of Biotite or other mineral. The spherical halos are produced by alpha particle radiation from the included uranium or thorium bearing species.

Thank you

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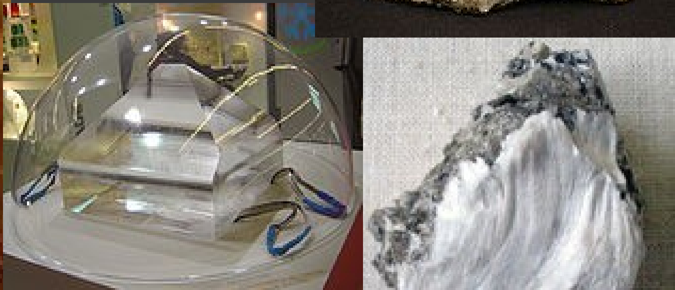

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