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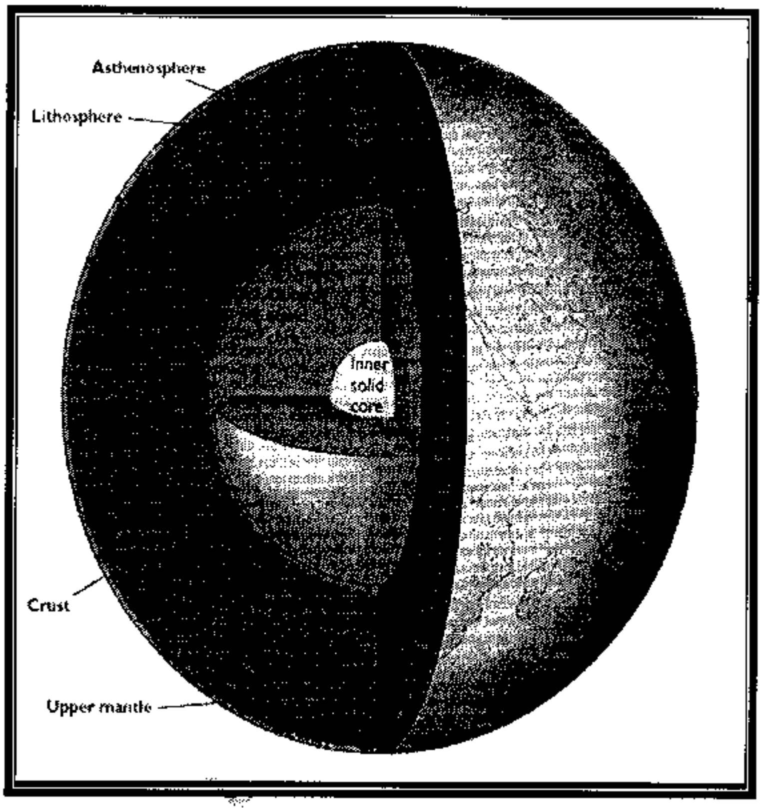
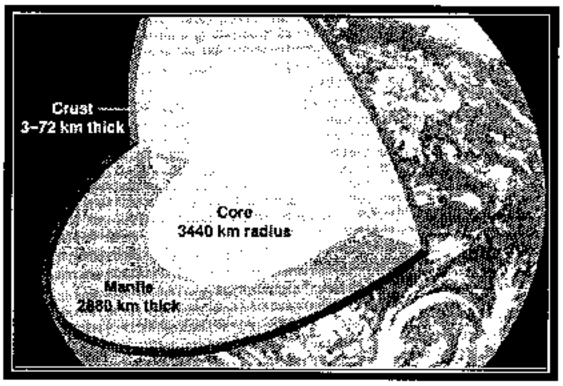
Lecture 1: Introduction of Geochemistry

- **Geochemistry**
- **Cosmochemistry**
- **The main focus of geochemistry**
- **Some subsets of geochemistry**

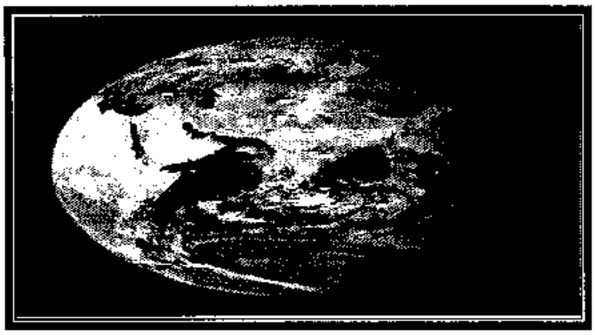


Geochemistry = chemistry of the Earth
(i.e., of earth materials — minerals and rocks)

- **Geochemistry**: is the science concerned with the chemistry of the earth. It deals with the distribution and migration of the chemical elements within the earth.



- **Cosmochemistry**: is the science of the occurrence and distribution of the elements in the universe.



- **The main focus of geochemistry is to:**

- Understand the principles governing the distribution and re-distribution of elements, ionic species and isotope ratios in earth materials, so that we can interpret the formation of mineral assemblages: conditions (P, T, etc.), processes (magmatic crystallization, weathering, chemical precipitation, metamorphism, etc.), and even the age.

- The field of **geochemistry** involves:

1. Study of the chemical composition of the Earth and other planets.
2. Study of the chemical processes and reactions that govern the composition of rocks, water, and soils.

- V.M. **Goldschmidt**, who is regarded as the founder of modern geochemistry, characterized geochemistry with the following words:

- The major task of geochemistry is to investigate the composition of the Earth as a whole and of its various components and to uncover the laws that control the distribution of the various elements.
- To solve these problems, the geochemist needs a comprehensive collection of analytical data of terrestrial material, i.e. rocks, waters and atmosphere.

- Based on **Goldschmidt** (1954) opinion:

a. The abundance of elements in rock, mineral or crystal.
b. The distribution of the elements.
c. Laws governing the abundance and distribution of elements in rock, mineral or crystal.

Some subsets of geochemistry are:

- **Isotope geochemistry:** Determination of the relative and absolute concentrations of the elements and their isotopes in the earth and on earth's surface.

- **Cosmochemistry**: Analysis of the distribution of elements and their isotopes in the cosmos.
- **Biogeochemistry**: Field of study focusing on the effect of life on the chemistry of the earth.
- **Organic geochemistry**: A study of the role of processes and compounds that are derived from living or once-living organisms.
- **Hydrogeochemistry**: Understanding the role of various elements in watersheds.
- **Environmental and exploration geochemistry**: Applications to environmental, hydrological and mineral exploration studies.

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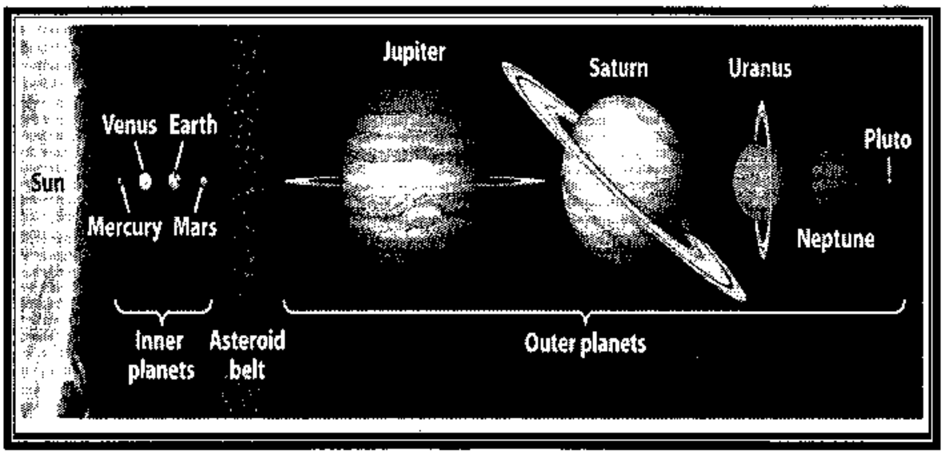
Lecture 2: Origin &Development of the Solid Earth

- **Universe & The Solar System**
- **The Origin of the Solar System**
- **The Nebular Hypothesis**
- **Planets**
- **The Layout of the Solar System**
- **Inner & Outer Planets**
- **The density of the Earth and Planets**
- **Relative Abundance of the Chemical Elements in the Solar System**



Universe & The Solar System

- **Universe**

What makes up the **universe**?

The Universe consists of a vast Space, within which are contained untold numbers of galaxies, billions of stars, planets, asteroids, and other celestial objects of varying sizes, shapes, and characteristics. Among the important members of the Universe are the galaxies.

- **The Solar System**

The sun, its eight planets, and their moons, together with smaller objects such as **asteroids** and **comets**, form the solar system.

The Origin of the Solar System

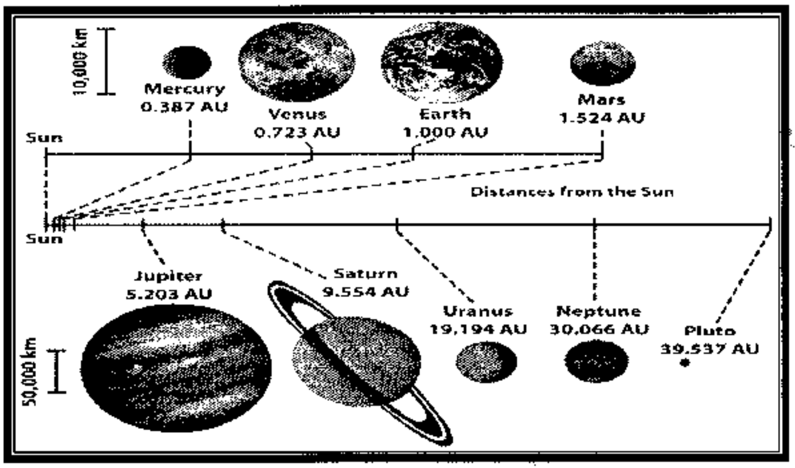
About 4.6 billion years ago, the solar system formed from a rotating cloud of interstellar matter. Eventually, as this cloud condensed, it collapsed under the influence of gravity and flattened into a rotating disk.

The Nebular Hypothesis

In 1755, the German philosopher Immanuel Kant suggested that the origin of the solar system could be traced to a rotating cloud of gas and fine dust.

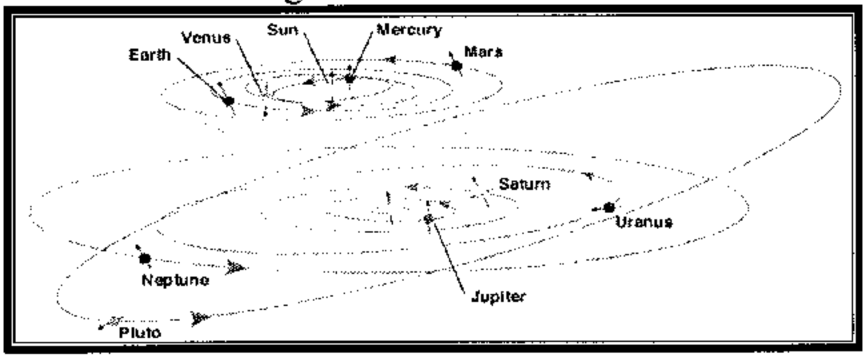
Planets

Different planets formed in different environments depending on their distance from the Sun.



The Layout of the Solar System

- All planets orbit the Sun in the same direction and in elliptical to circular orbits located in the same plane.
- The planets revolve around themselves in the same direction as the sun, except Venus and Uranus.
- Planets fall into two main categories: Inner Planets & Outer Planets.



Inner & Outer Planets

Terrestrial Planets (Inner Planets)

- They are the four planets closest to the sun.
- The four planets that orbit nearest to the sun are called terrestrial planets. Also referred to as the inner planets.
- The terrestrial planets are **Mercury, Venus, Earth, and Mars.**

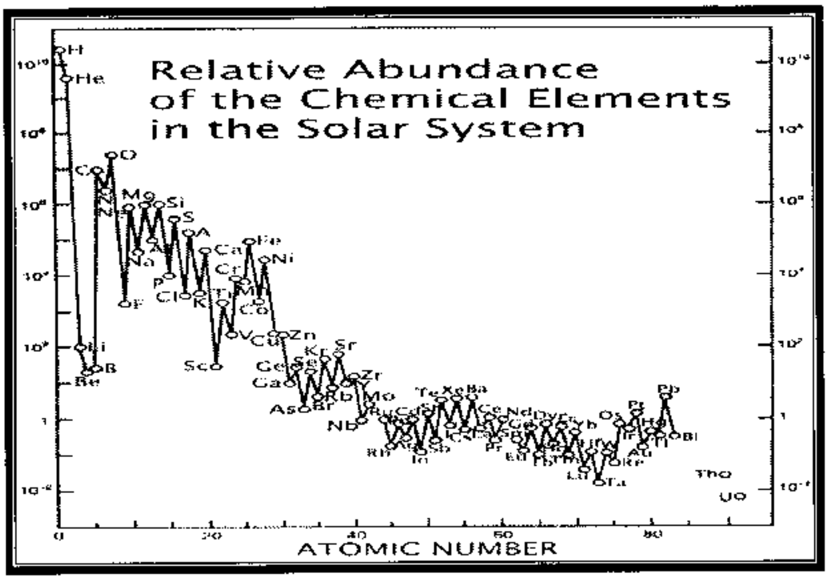
Gaseous Planets (Outer Planets)

The four planets that orbit farthest from the sun are called gas giant planets. The gas giant planets are **Jupiter, Saturn, Uranus, and Neptune.**

The density of the Earth and Planets

The density of Earth is 5.53 g/cm3. This is an average of all of the material on the planet. Earth is the densest planet in the Solar System; however, the second densest planet, Mercury. The density of Earth is calculated by dividing the plant's mass by its volume. Less dense materials (gases) could escape to greater distances from the sun e.g. Jupiter.

Relative Abundance of the Chemical Elements in the Solar System



From the figure, we see patterns:

1- An overwhelming abundance of light elements are hydrogen and then helium (H, He).
2- Cosmic abundance decreases in an almost exponential manner with increasing the atomic number and up to the element in atomic number (45).
3- Elements Lithium, Beryllium, and Boron are very low in relative abundance.

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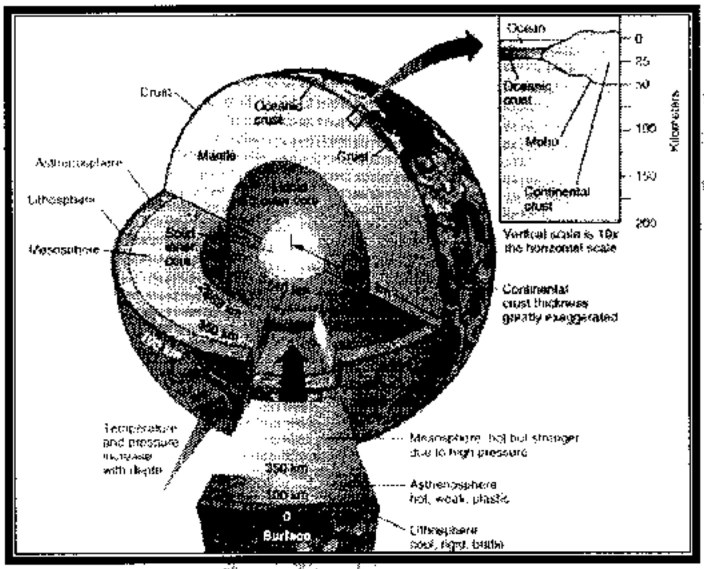
Lecture 3: Earth's Spheres & Earth's Interior

- **Earth's Spheres**
- **Earth's Compositional Layers**
- **Earth's Interior**
- **The lithosphere and asthenosphere**
- **Seismology came to verify the layering of the Earth**



Earth's Spheres

1. **Hydrosphere:** The water portion of our planet.
2. **Atmosphere:** The gaseous portion of a planet; the planet's envelope of air.
3. **Biosphere:** The totality of life on earth; the parts of the solid earth, hydrosphere, and atmosphere in which living organisms can be found.
4. **Geosphere:** The solid earth, the largest of Earth's four major spheres.

Earth's Compositional Layers

- The abundance of an element is the amount of that element in a particular region of the natural world.

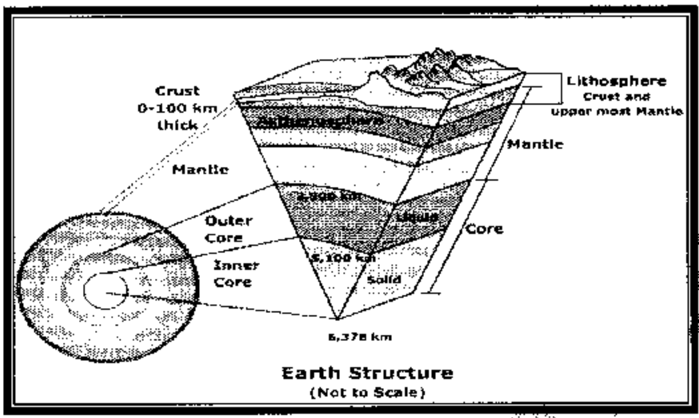
- Elements are not equally abundant in all regions – abundances differ due to the differences in physical and chemical behavior of the elements.

- Six elements (out of more than 100) make up 99% of Earth's mass.

Earth's Interior

Early in earth's history, the sorting of material by compositional (and density) differences resulted in the formation of three layers:

1. **Crust**
2. **Mantle**
3. **Core**



Earth Structure
(Not to Scale)

1. **Crust:** The Earth's crust is a thin layer of rock that floats on the mantle.
2. **Mantle:** The layer of Earth located below the crust. Mostly solid and made up of Ca, Fe, Mg, Si, O.

3.Core: Located beneath the mantle, it is the innermost layer of earth. The composition of the core is thought to be an iron-nickel.

The lithosphere and asthenosphere

Lithosphere: is the relatively rigid layer that lies between the surface and a depth of about 100-150 km.

Asthenosphere: is the relatively soft layer that lies below a depth of 100-150 km.

Seismology came to verify the layering of the Earth

There are two basic types of body waves to explore the Earth's interior:

- P (Primary) Waves

Compressional waves (P waves) expand and compress as they travel through solid, liquid, or gas.

Compressional Primary (P) Waves:

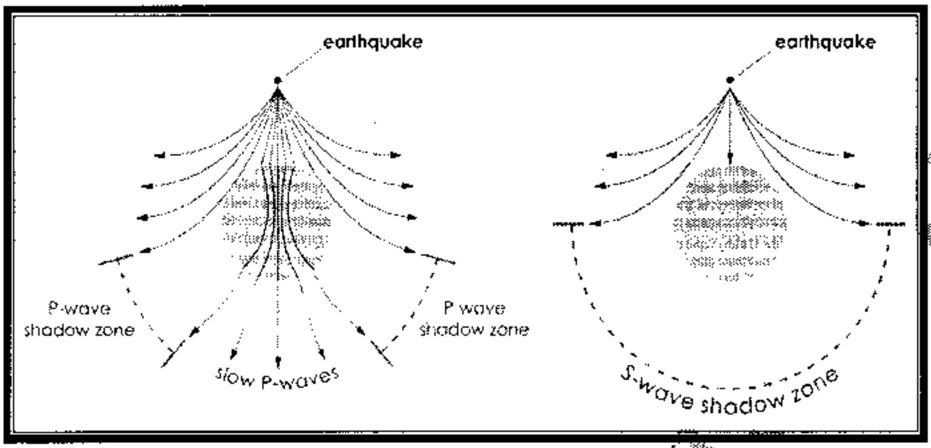
- Travel through solids and liquids.
- Travel speed increases with material density.

- S (Secondary) Waves

Shear waves (S waves) involves side-to-side motion (shearing). Shear waves can propagate only through solids and not through fluids.

Shearing Secondary (S) Waves:

- Travel through solids but not liquids.
- Travel speed increases with material density.



Moho discontinuity: It is the boundary between the Earth's crust and mantle. It is identified by a change in the velocity of seismic waves passing through the Earth.

Gutenberg discontinuity: The Gutenberg discontinuity separates the mantle and the core, where there is an abrupt change in the seismic waves that travel through Earth.

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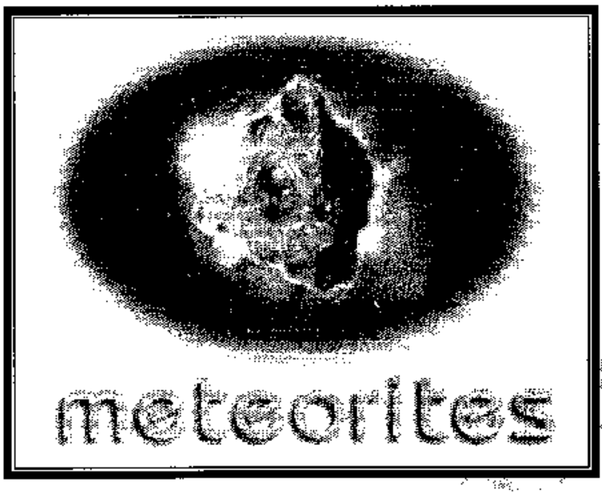
Lecture 4: Meteorites

- **Meteorite**
- **Meteor**
- **Meteorites Classification**



Meteorite: a rock from space that lands on the Earth.
Meteor: a flash of light caused when a particle from space burns up upon entering our atmosphere.
Meteorites provide information about the chemical and physical properties at different locations within the Solar Nebular disk.

Meteorites Classification

1. Stony Meteorites (Aerolites): **(92.8%)**
Stony meteorites are divided into subclasses **Chondrites & Achondrites**.

A. **Chondrites**: (It forms **90%**)
Chondrites are one of the **Stony Meteorites**, formed when various types of dust and small grains that were present in the early solar system accreted to form primitive asteroids.

i. **Carbonaceous**
Carbonaceous chondrites contain volatile elements.
ii. **Enstatite**
Enstatite chondrites contain refractory elements.
B. **Achondrites**: (It forms **10%**)

Achondrites are also stony meteorites. They are formed by melting and recrystallization on or within meteorite parent bodies; as a result, Achondrites have distinct textures and mineralogies indicative of igneous processes.

*Table 1: Average **mineral composition** of the **Stony Meteorites**.*

Minerals	**Chondrites %**	**Achondrites %**
Ni-Fe	12	1
Olivine	46	9
Hypersthene	21	50
Diopside	4	12
Plagioclase	11	25
Total	94	79

*Table 2: Average **chemical composition** of the **Stony Meteorites**.*

Chemical components	**Chondrites %**	**Achondrites %**
Silica fraction $SiO_2+MgO+Fe_2O_3+Al_2O_3+CaO$	75.42	95.78
Metal fraction Fe+Ni+Co+P	18.9	2.46
Troilite: FeS	5.35	1.25

2. Iron Meteorites (Siderites): (5.7%)

Iron Meteorites, also known as siderites, or ferrous meteorites, are a type of meteorites that consist overwhelmingly of an **iron-nickel alloy** (Kamacite).

3. Stony- Iron Meteorites (Siderolites):(**1.5%**)

Stony-Iron Meteorites consist of a high content of coarse Kamacite and silicates minerals like olivine and pyroxene.

According to the texture, **Stony- Iron Meteorites** divided into **two** groups:

A. Pallasites group:

Consist of **Kamacite** (25-60%) and **Olivine** (35-75%). It forms from continuous matrix.

B. Siderophyre group:

Consist of **Kamacite** (50%), **Plagioclase**, **Feldspar**, **Pyroxene** and **Olivine**. It forms from discontinuous matrix.

Lunar Meteorites

Lunar Meteorites are rocks found on earth that were ejected from the moon by the impact of an asteroidal meteoroid or possibly a comet. meteoroids strike the moon every day. some ejected material becomes captured by the earth's gravitational field and lands on earth.

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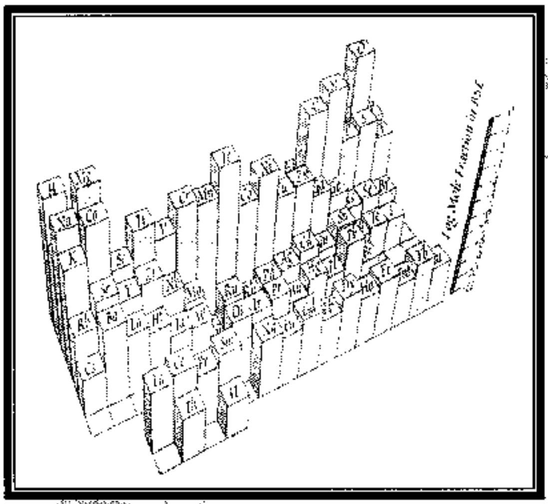
Lecture 5: Geochemical Classification of the elements

- **Geochemical classification of the elements**
- **Chemical elements can be classified according to their geochemical affinity into the following groups:**
- **Geochemical classification of the elements depending on their distribution in meteorites.**
- **Groups of chemical elements and heat of formation of their oxides**
- **The geochemical properties of the elements and the type of bonds**
- **Based on the electronegativity properties, the elements are classified into three groups as follows:**



- **Geochemical classification of the elements**

- The chemical elements are distributed in patterns that depend on the phases or the nature of the materials available in the different parts of the earth.
- (**Goldschmidt**) was the first to develop basic concepts for the geochemical classification of elements based on their distribution in the constituent phases of meteorites as well as observing their distribution during the melting of some ores such as slate rocks bearing copper ore.

- ***Chemical elements can be classified according to their geochemical affinity into the following groups:***

1. Siderophile: Represents the elements that have an affinity to exist with the iron metal or in the free metallic phases.

2. Chalcophile: It includes the elements that have an affinity to combine with sulfur and form the sulfide phases.

3. Lithophile: The elements that have the ability to combine with oxygen in the phases of oxides, silicates, carbonates .... etc., that is, excluding the sulfide and metallic phases.

4. Atmophile: It includes elements that have an affinity to exist in the gaseous state, i.e. in the atmosphere.

- **Geochemical classification of the elements depending on their distribution in meteorites.**

- The table displays the elements' totals according to the geochemical classification and on the chemical data of the meteorites.

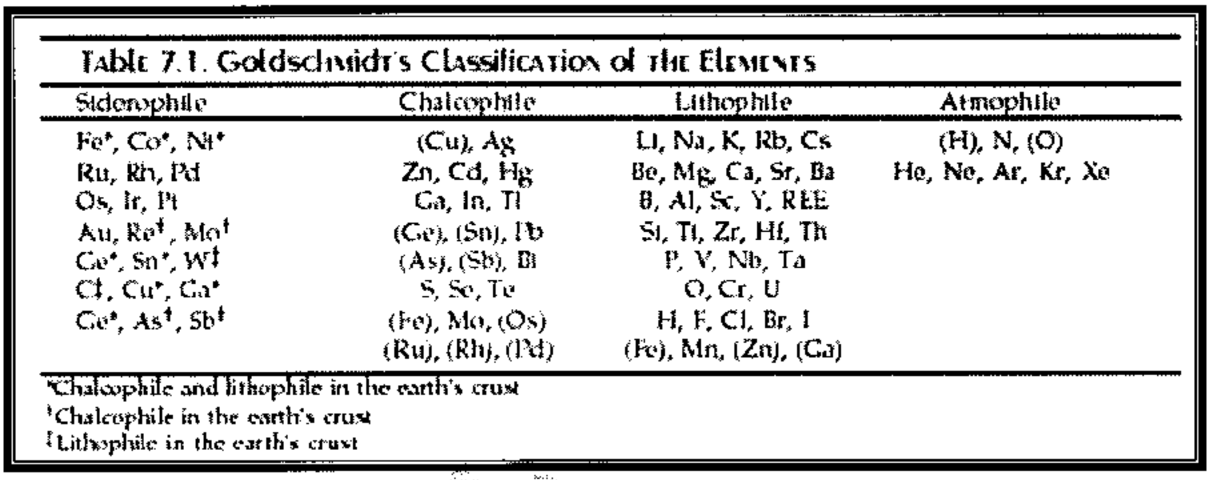


Table 7.1. Goldschmidt's Classification of the Elements

Siderophile	Chalcophile	Lithophile	Atmophile
Fe*, Co*, Ni*	(Cu), Ag	Li, Na, K, Rb, Cs	(H), N, (O)
Ru, Rh, Pd	Zn, Cd, Hg	Be, Mg, Ca, Sr, Ba	He, Ne, Ar, Kr, Xe
Os, Ir, Pt	Ga, In, Tl	B, Al, Sc, Y, REE	
Au, Re†, Mo†	(Ge), (Sn), Pb	Si, Ti, Zr, Hf, Th	
Ge*, Sn*, W‡	(As), (Sb), Bi	P, V, Nb, Ta	
C‡, Cu*, Ga*	S, Se, Te	O, Cr, U	
Ge*, As†, Sb†	(Fe), Mo, (Os)	H, F, Cl, Br, I	
	(Ru), (Rh), (Pd)	(Fe), Mn, (Zn), (Ga)	

*Chalcophile and lithophile in the earth's crust

†Chalcophile in the earth's crust

‡Lithophile in the earth's crust

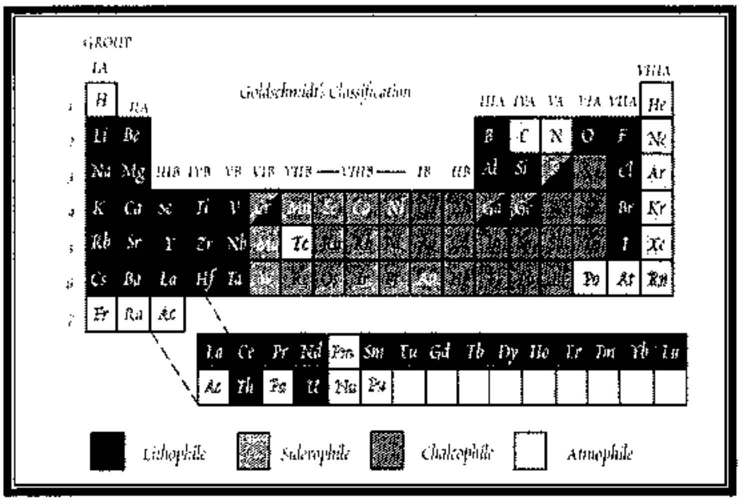
- **Geochemical classification of the elements and their position in the Periodic Table.**

- The different geochemical characteristics of the elements are governed by the composition of their atoms and thus their position on the periodic table.

- **Lithophile** elements are concentrated on the **left** side of the periodic table, and their ions contain eight electrons in their outermost orbit.

- Most of the **Siderophile** elements are located roughly in the **center** of the periodic table, as well as some elements of neighboring groups.

- **Chalcophile** elements are concentrated on the **right** side of the periodic table, and their ions contain (18) electrons in the outer orbit.



- **Groups of chemical elements and heat of formation of their oxides**
  Groups of elements can also be distinguished on the basis of the heat of their oxides formation. The **lithophile** elements are those whose oxides have more heat formation than ferrous oxide formation.
- **The geochemical properties of the elements and the type of bonds**

- The geochemical properties of the elements vary according to the type of bonds (metallic, covalent, and ionic) with which it is associated in the mineral phase.

- A number of studies have dealt with the relationship between the nature of the element to which the element is associated with the chemical and physical properties that can be quantified such as the melting temperature of the elemental phases, the temperature of the composition of the elements compounds, the refractive index of light in the elements of the elements, the ionization potential, and the Electronegativity of ions elements.

Based on the electronegativity properties, the elements are classified into three groups as follows:

1. Elements with values of (1.6) and less, and show a tendency to form ionic bonds with oxygen, and these elements possess a **lithophile** property.
2. Elements with values ranging from (1.7-2.0), and form covalent bonds with sulfur, and these elements are **Chalcophile**.
3. Elements with values ranging from (2.0-3.0), and are related to metal bonds, and these elements belong to the **Siderophile** group.

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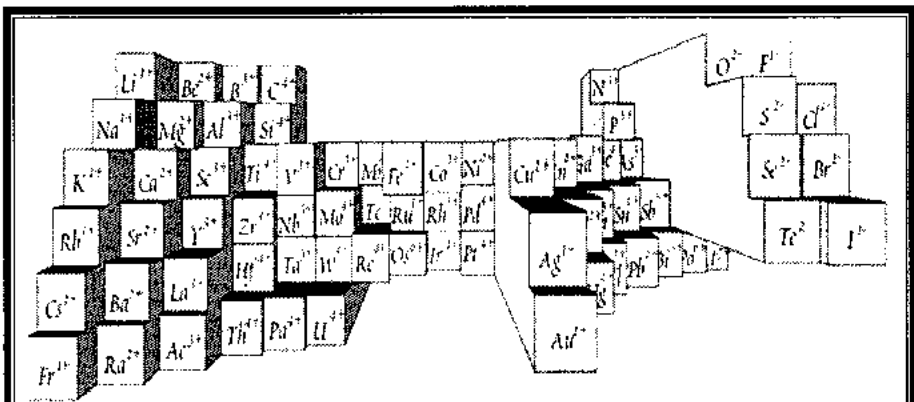
Lecture 6: <u>Chemical Weathering & Ionic Potential</u>

- **Weathering**
- **Chemical weathering**
- **Chemical Weathering processes**
- **Ionic potential**
- **Sorption**



Ionic Radii

Weathering: the disintegration and decomposition of rock at Earth's surface. There are two types of weathering:

- **Mechanical weathering:** the physical disintegration of rock, resulting in smaller fragments.
- **Chemical weathering:** the processes by which the internal structure of a mineral is altered by the removal and\ or addition of elements.

Chemical Weathering processes:

The reactions that occur when water comes into contact with rocks (minerals) can be illustrated as follows:

Hydrolysis: the chemical reaction between the Hydrogen (H^+) ions and Hydroxyl (OH^-) ions of water and a mineral's ions.

Hydration: This reaction includes adding water molecules to the composition of some minerals, as is the case for ferric oxide (hematite) and calcium sulfate (anhydrite).

Oxidation: is the combination of Oxygen with other elements and compounds. Some minerals are chemically weathered through the oxidation of their components such as ferrous, free sulfur, negative ion (S^{2-}) and manganese ion (Mn^{2+}).

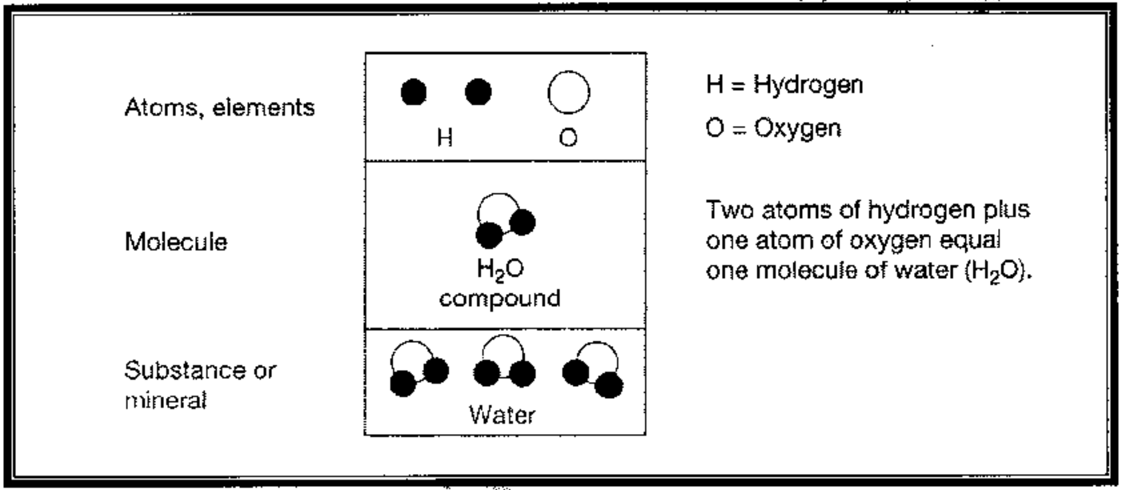
Carbonation: is the combination of elements and compounds with Carbon dioxide. It is the reaction of carbonic acid in water with minerals.

Solution: is the separation of the ions of a substance in a liquid, and the solid substance dissolves.

Ionic potential

- **Ionic potential**: is defined as the result of dividing the **charge** of the ion (**z**) by the **radius** of the ion (**r**).

$$\textbf{Ionic potential} = \frac{\underline{\textbf{Ionic charge (z)}}}{\textbf{Ionic radius (r)}}$$



- *The elements are divided into* ***three*** *main groups depending on the* ***ionic potential****:*

1. Elements with low ionic potential (**Ca, Na**) are soluble as simple cations. (Elements with ionic potential less than **3**)
2. Elements with very high ionic potential attract Oxygen ions and form soluble Oxy-anions (**PO_4^{-3}, SO_4^{-2}**). (Elements with ionic potential more than **12**)
3. Elements with intermediate ionic potential are generally immobile become of very low solubility and strong adsorption to surfaces (**Al, Ti, Sn**). (Medium ionic potential elements **3-12**)

- **Sorption:** removal of solutes from solution onto mineral surfaces.

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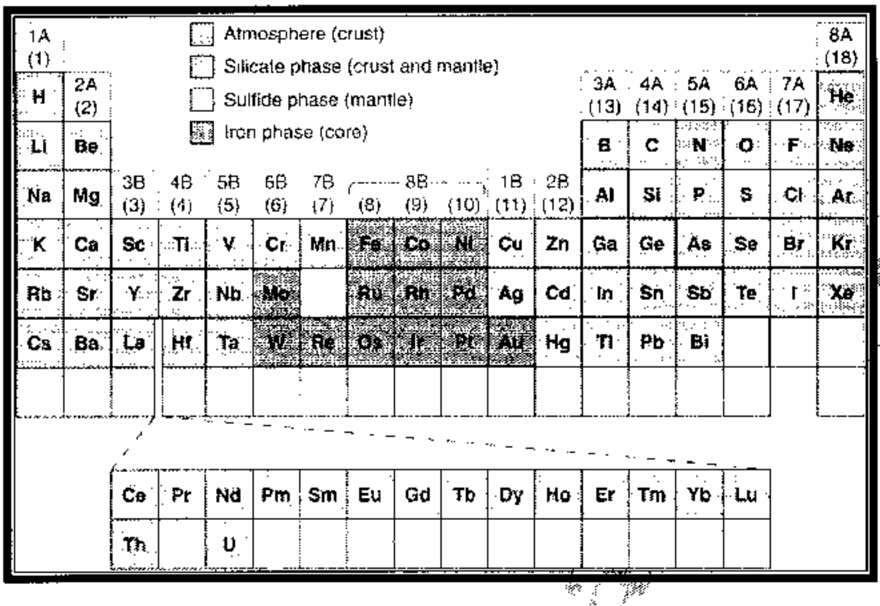
Lecture 7: Trace Element Geochemistry

- **Trace Element Geochemistry**
- **Ionic Substitution**

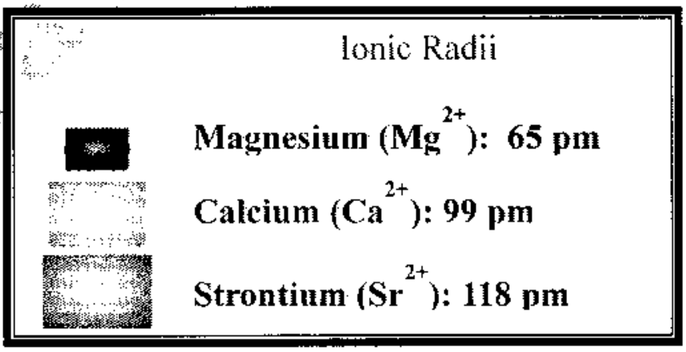


Trace Element Geochemistry

- Ionic Substitution depends on two factors:
  - **Ionic radius**
  - **Ionic charge**

Effect of Ionic Radius and Charge

- The greater the difference in charge of radius between the ion normally in the site and the ion being substituted, the more difficult the substitution.



Ionic Substitution

1) Radii differ by less than **15%**.
2) Charge difference of **one** unit substitutes as long as electrical neutrality is maintained.

3) Ion with **higher ionic potential** forms a stronger bond with surrounding ions.
4) Even when **size** and **charge** are satisfied, competing ions with different **electronegativites** that from bond of different ionic character may not substitute.

Q/ What are the types of **ionic substitution** in **trace elements**?

1. **Camouflage**: occurs when the minor element has the same charge and similar ionic radius as the major element (same ionic potential).
   IP(minor)= IP(major)
2. **Capture**: occurs when a minor element enters a crystal preferentially to the major element, because it has a higher ionic potential than the major element.
   IP(minor)> IP(major)
3. **Admission**: Involves entry of a foreign ion with an ionic potential less than that of the major ion.
   IP(minor)< IP(major)

Compatible Elements: elements that fit easily into rock-forming minerals. e.g. **(Cr, V, Ni)**
Incompatible Elements: elements that are too large and/or highly charged to fit easily into common rock-forming minerals. e.g. **(K^+, Rb^+, Zr^{+4}, Hf^{+4})**

- **Large-Ion Lithophile Elements (LILE) or Low-Field Strength Elements (LFSE)**

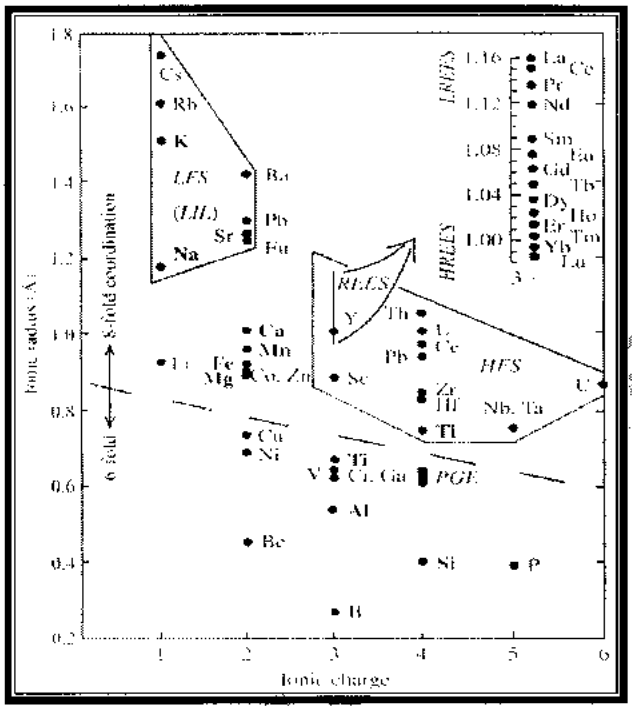
The element of large ionic radius and with a valency of 1 or 2 (e.g. Rb^{2+}, Pb^{2+}, and Ba^{2+}), which during igneous fractionation tends to be concentrated in silicic melt, and from which LILE are incorporated mainly into potassium silicates such as the alkali feldspars and micas.

Q/ What are the characteristics of the **large-ion lithophile (LIL)**?

1) Ions become sorted by size and charge during crystallization of a cooling magma.
2) Ions not fitting into the major rock forming minerals are called incompatible.
3) Greater charge difference resulted in problems maintaining electrical neutrality:
   i. Coupled substitution.
   ii. Adsoption.

- **High-Field Strength Elements (HFSE)**

Although these elements do not have large ionic radius, because of their high charge and the consequent difficulty in achieving charge balance, they are typically incompatible (**Ti, Zr, Hf, Nb** and **Ta**).



NB 1 Å = 10^{-10} meters = 100 pm

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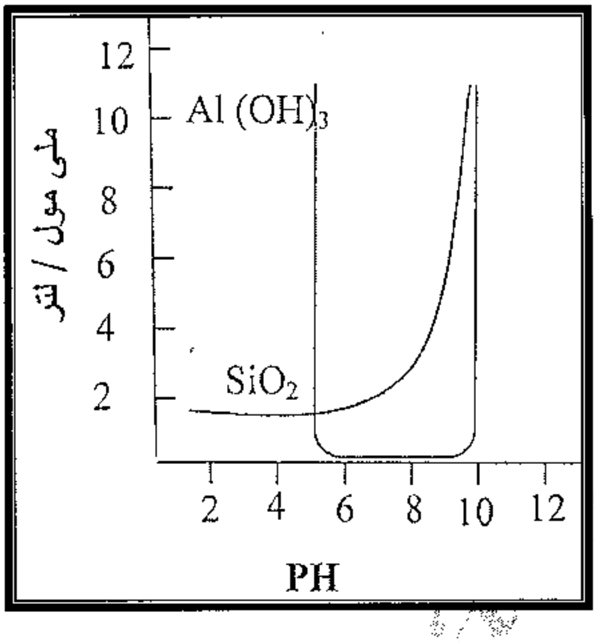
Lecture 8: Physicochemical Factor in Sedimentation

➢ Physicochemical Factor in Sedimentation



Physicochemical Factor in Sedimentation

There are four main factors that affect the sedimentation process in sedimentary rocks, and these four factors are:

1) Ionic Potential
2) Hydrogen-Ion Concentration (pH)
3) Oxidation-Reduction Potentials (Eh)
4) Colloids and Colloidal Processes

1) Ionic Potential

2) Hydrogen-Ion Concentration (pH)

We can get correct numbers when we use the negative logarithm of the hydrogen ion concentration (negative logarithm of H^+), which is known as the pH number and symbolized by pH.

$$\mathbf{pH = - Log\ H^+}$$

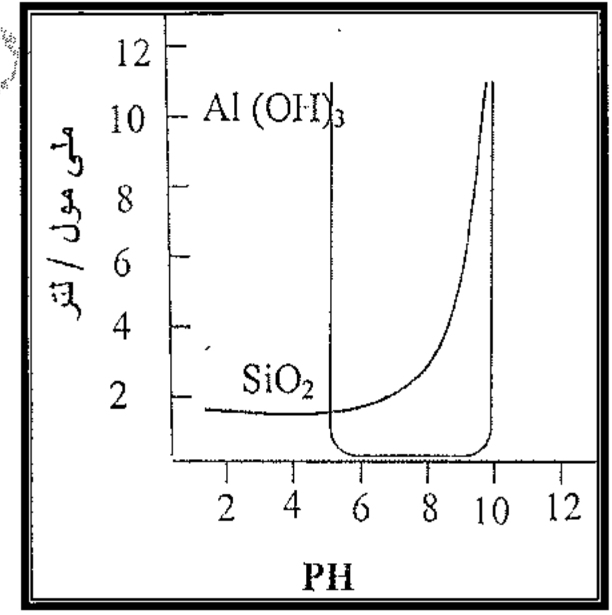
On this basis, the **pH** of very strong acids is (**zero**) i.e. **pH = 0**, and for neutral solution it is (7) i.e. **pH = 7 (pH = - Log 10^{-7}** = 7), and for the base solution it is **pH = 14.**

The product of multiplying the hydrogen ion concentration and the hydroxide ion concentration is constant for all solutions and is equal to **10^{-14}** mol / liter. This means that the acidity or basicity of any solution can be expressed either by the concentration of hydrogen ion or hydroxyl ion. The reason for this is that the hydroxyl ion is found in strong acid solutions, and this presence may be in a very low concentration, but it is sufficient to keep the product of the hydrogen and hydroxyl concentration equal to **10^{-14}** mol / liter.

We get that the ferric ion concentration in the solution is in direct proportion to the cube of the hydrogen ion concentration. The following table displays the ferric ion concentrations at different **pH** values. It is evident that ferric ion concentrations increase by a hundred thousand times in aqueous solutions with an acidic function of **6** compared to solutions with an acidic function of **8.5**.

pH	Amount
8.5	3.10^{-8} mg/m^3
8	4.10^{-7} mg/m^3
7	4.10^{-5} mg/m^3
6	5.10^{-3} mg/m^3

- Both silica and aluminum minerals in solutions are significantly affected by **pH** values during the weathering process, transport and sedimentation (re-sedimentation), and to explain this process, the following drawing shows how aluminum hydroxide and silica are dissolved depending on the **pH**.



- At **pH** levels less than **4**, aluminum is melted, while silica has a low melting point (low solubility). At this **pH**, the aluminum will dissolve in the solutions while the silica remains in place (in the source rocks), insoluble or slightly soluble. These natural conditions seldom exist for sedimentary rocks with a **pH** less than **4**.

- At a **pH** between **(5-9)**, the solubility of silica increases, but the aluminum is insoluble under these conditions. In these conditions the silica is raised, leaving the aluminum undissolved. It is these conditions that are responsible for the formation of laterite and bauxite deposits.

3) Oxidation-Reduction Potentials (Eh)

- Many elements exist in different states of oxidation state in the earth's crust. For example, iron exists in the form of elemental metal (**native metal**) and carries the **Oxidation State = 0** (zero), as well as exists in the form of **ferrous** and carries **Oxidation State = 2**, as well as in the form of **ferric** and carries the **Oxidation State = 3**. Any iron: $\mathbf{Fe^{0}}$, $\mathbf{Fe^{+2}}$, $\mathbf{Fe^{+3}}$.

Likewise, they have different oxidation states, such as **Manganese**: $\mathbf{Mn^{+2}}$, $\mathbf{Mn^{+3}}$, $\mathbf{Mn^{+4}}$ **Sulfur**: S^{0}, S^{+6}, S^{-2} and **Vanadium**: V^{+5}, V^{+4}, V^{+3} and **Copper**: $\mathbf{Cu^{0}}$, $\mathbf{Cu^{+1}}$, $\mathbf{Cu^{+2}}$, and **Cobalt**: $\mathbf{Co^{+3}}$, $\mathbf{Co^{+2}}$, and **Nitrogen**: N^{0}, N^{+5}, N^{-3}.

- The stability of an element to exist in a specific state of oxidation (**Particle Oxidation State**) depends on the energy change when electrons are raised or added. The **quantitative measurement** of this change in energy gives us a number called by many names, namely:
  1- Oxidation – Redox Potential
  2- Oxidation Potential
  3- Redox Potential

  It is often preferred to use the **Oxidation Potential**, denoted by **Eh**.

- The oxidation and reduction potential is a function that expresses the ability of natural environments to oxidize and reduce the materials they contain. This function is practically measured by dipping an inert electrode, usually made of platinum, in the environment in which the oxidation and reduction potential is to be measured, such as river and sea water, soils or swamps. The oxidation-reduction potential of any reaction is of relative value. If we consider that the next interaction is an ideal interaction.

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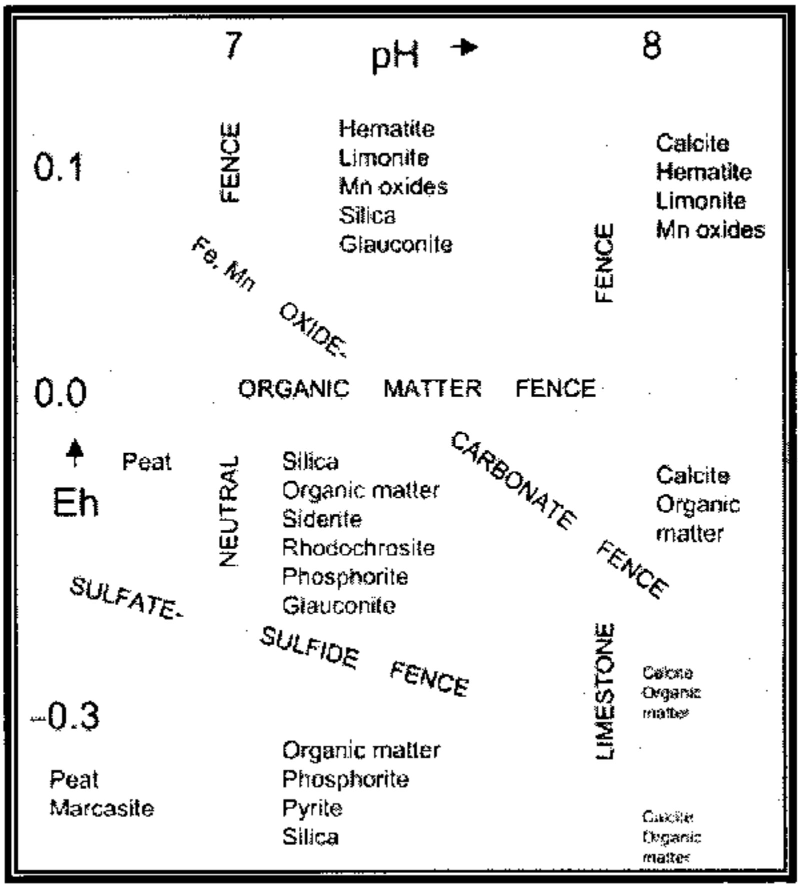
Lecture 9: - Relationship between Oxidation potential (Eh) and (pH)
- Colloids and Colloidal Processes



- **Relationship between Oxidation potential (Eh) and (pH)**

- Surface environments contain different types of water with different values of the acidic function, but most of them are limited to the range (**4-9**). The acidic function (**pH**) may be reached in certain areas **less than** (**4**), as is the case in waters of volcanic events or in mine waters of sulphide deposits. In other areas, it may also reach **more than** (**9**), as is the case in the water drainage systems of Ultrabasic(Ultramafic) rock outcrops.
- As for the **Oxidation-Reduction Potential** (**Eh**), its range is determined in sedimentary environments by the values of the voltage of the following **two** reactions:

1) $H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e$ **E°= 1.23 volt**

2) $2H + 2e \longrightarrow H_2$ **E°= zero volt**

- Equations (**1**) and (**2**) clarify that the most powerful oxidizing agent in surface environments is **oxygen**, and that the presence of any other factor that has an oxidation voltage greater than reaction (1) will lead to the dissolution of water and the liberation of **oxygen**. The strongest reducing agent in surface environments is also **hydrogen**, and the presence of any other factor that has an oxidation potential less than reaction (2) will lead to the dissolution of water and the liberation of **hydrogen**.

- **Geochemical Fence**

- Both the oxidation potential (**Eh**) and (**pH**) are among the basic rules in determining the nature of many products of sedimentary processes (**sediments**).

- As for the **geochemical fences,** they are as follows:

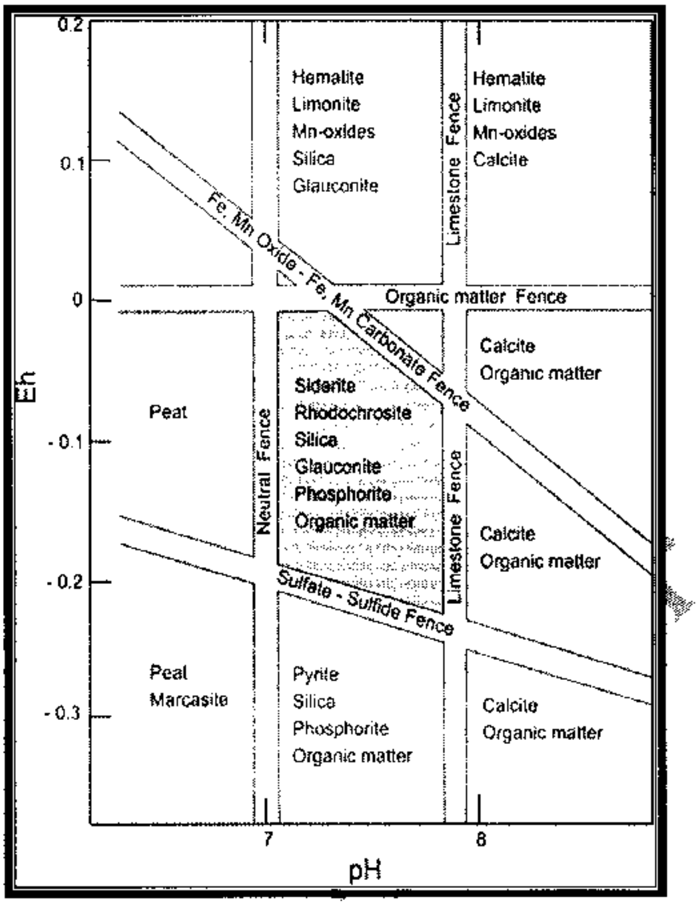
1. Neutral fence: It is set at (**pH** = 7), and the conditions are basic to the right of the fence and acidic to the left of it.

2. Limestone fence: It is specified with a value of (**pH = 7.8**), and to the right of the fence, **pH** values are higher than (**7.8**), so the **Calcite** mineral will deposit (**Rigidity deposited**), and to the left of it will be (**pH**) values. Less than (**7.8**), the calcite will be dissolved (remain in the solution, and the calcite will not crystallize except when the **pH** values are higher than (**7.8**).

3. Organic Matter Fence: It is defined by the oxidation voltage value (**Eh = 0**), and below this fence the organic materials are stable with values less than **zero** (**Negative -**), and at a level higher than this fence with values more than **zero** (**Positive +**), the organic matter will be oxidized to carbon dioxide (**CO_2**).

4. The Sulphate-Sulphide fence: Which is determined by the oxidation and reduction effort of Sulphides-sulphates, and above this fence are sulphates or sulphates precipitates, and below it, sulphates precipitate, so we see **Pyrite** and **Marcasite** minerals precipitates below.

5. Fe, Mn Oxide - carbonate fence: This fence is determined by the oxidation and reduction effort, at which the ferrous and manganese compounds are oxidized to higher oxides, the iron is below (**Fe^{2+}**) and is at the top (**Fe^{3+}**).



- **Colloids and Colloidal Processes**

- The term colloids are used, which are a case of very small sedimentary granule sizes whose size ranges between **10^{-3}-10^{-6}** mm. The colloidal solutions interfere with the regular solutions and it is difficult to differentiate between them.
- In sedimentary processes, **colloidal solutions** are divided into **three** categories:

1) Sols: colloidal substances are present in small quantities in the liquid, so that the solution attached to them is similar to the liquid with its physical properties (its solution flows quickly without any obstruction (**Rigidity**).

2) Gels: the quantities of colloidal substances increase, and their solutions are similar to the gelatinous solution (there is some obstruction (**Rigidity**) when the flow of the solution exists.

3) Pastes: the quantities of colloidal substances are large, so that their solution resembles dough solutions similar to **plastic clays**.

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Lecture 10: <u>Hydrochemistry</u>

- **Physical & Physico-Chemical Tests**
- **Metallic Ions**

The variables are presented under four main headings:

- **Physical and Physico-chemical**
- **Metallic elements**
- **Non-metallic constituents**
- **Organic constituents**

Physical & Physico-Chemical Tests

1. Temperature

In limnological studies, the temperature at different depths is measured. Data on the water temperature are necessary for cooling purposes or for processes used in industry, as well as for the calculation of the solubility of oxygen and the carbon dioxide-bicarbonate-carbonate equilibrium. Identification of die water sources, such as deep wells, is often possible by temperature measurement alone.

2. pH

The pH of water approximates the activity of free hydrogen ions in water. It is defined as the negative logarithm of the hydrogen ion concentration. The practical pH scale extends from **0** (very acidic) to **14** (very alkaline) with the value of **7** corresponding to exact neutrality at **25°C**.

The pH of natural waters is dictated to some extent by the geology of the watershed and is governed by the carbon dioxide/bicarbonate/carbonate equilibria. The range in pH for most waters is between **4.5** and **8.5** which encompasses the pH value of **5.6** for rainwater in equilibrium with atmospheric $\mathbf{CO_2}$.

3. Electrical Conductivity

Electrical conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, their total concentration, mobility, valence, and relative concentrations, and on the temperature of measurement. Solutions of most inorganic acids, bases, and salts are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in an aqueous solution conduct a current poorly, if at all.

Estimates of total dissolved solids can be made by multiplying the conductivity value by an empirical factor dependent upon the soluble components of the water and the sample temperature.

Table (1) The relationship between electrical conductivity and water mineralization.

E.C. µs/cm	Mineralization
<100	**Very Weakly Mineralized Water (Granite terrain's)**
100 – 200	**Weakly Mineralized Water**
200 – 400	**Slightly Mineralized Water (Limestone terrain's)**
400 – 600	**Moderately Mineralized Water**
600 – 1000	**Highly Mineralized Water**
>1000	**Excessively Mineralized Water**

4.Total Dissolved Solids (TDS)

Refer to any minerals, salts, metals, cations, or anions dissolved in water. Basically, the total dissolved solids are the sum of the cations and anions in the water. when TDS levels exceed 1000 mg/L it is generally considered unfit for human consumption. It can be measured by mg/l or ppm.

Table (2) classification of water according to the total dissolved solids (T.D.S.)

Water Class	Davis and Dewiest,1966 T.D.S. (ppm)	Drever,1997 T.D.S. (ppm)
Fresh Water	0 – 1000	< 1000
Brackish Water	1000 – 10000	1000 – 20000
Salty Water	10000 – 100000	-
Saline Water	-	35000
Brine Water	>100000	> 35000

5. Total Suspended Solids (TSS)

Suspended solids are composed of day, sand, silt, finely divided organic and inorganic matter, plankton, and other microorganisms in water. The concentration of suspended solids is related to seasonal factors and flow regimes and is affected by snowmelt and rain events.

6. Transparency

Water transparency or clarity is a function of the concentration of suspended solids in the water column. A marked attenuation in light intensity with depth in turbid waters will result in greater absorption of solar energy near the surface. The warmer surface water may reduce oxygen transfer from the air to the water and will decrease density and stabilize stratification thus slowing or precluding vertical mixing.

- **Metallic Ions**

1- Alkali Metals (Na, K)

Sodium is one of the more abundant elements and is a common constituent of natural waters. Concentrations range from very low values in surface waters draining highly weathered environments to relatively high values in deep groundwater's to a very high values in marine waters. **Sodium** at a concentration of **10.77** mg/g (salinity= **35** g/kg) is the most abundant metal ion in seawater. While **potassium** ranks seventh in elemental abundance its concentration in most natural waters remains relatively low, seldom reaching **(2)** mg/liter in drinking-water.

2- Alkaline- Earth Metals (Ca, Mg)

Calcium dissolves out from practically all rocks and is consequently detected in all waters. Waters associated with granite or siliceous sand may contain less than **(10)** mg of **calcium** per liter.

Magnesium is a relatively abundant element in the earth's crust and, hence, a common constituent of natural water. Waters associated with granite or siliceous sand may contain less than **(5)** mg of **magnesium** per liter.

3- Trace Metals (Al, Cr, Fe, Hg, Mn, Ni, Pb, Zn, Cd, Cu)

The speciation and bioavailability of trace metals in water are controlled by physical and chemical interactions and equilibria. These interactions are affected by many factors, including **pH**, redox, temperature, hardness, $\mathbf{CO_2}$ concentrations, the type and concentration of available ligands and chelating agents and type and concentrations of metal ions.

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Lecture 11: Hydrochemistry/ Non-Metallic Constituents

The variables are presented under four main headings:
- **Physical and Physico-chemical**
- **Metallic elements**
- **Non-metallic constituents**
- **Organic constituents**

- **Non-metallic constituents**

- **Alkalinity**

The **alkalinity** of a natural or treated water is the capacity of some of its components to accept protons (to bind an equivalent amount of a strong add). Examples of such components are hydroxyl ions and anions of weak adds, e.g. bicarbonate, carbonate, phosphate, silicate. The equivalent amount of a strong add needed to neutralize these ions gives the total alkalinity (T).

- **Arsenic**

Arsenic is poisonous and severe toxicity has been reported after ingestion of only **(100)** mg of the element. **Arsenic** is not geologically uncommon and occurs in natural water as arsenate (**AsO_4**) and arsenite (**AsO_2**).

- **Boron**

In most natural waters boron is rarely found in concentrations greater than **(1)** mg/1, but even this low concentration can have deleterious effects on certain agricultural products including citrus fruits, walnuts, and beans.

- **Chloride**

Chloride anion is generally present in natural waters. A high concentration occurs in waters from chloride-containing geological formations. Otherwise, a high **chloride** content may indicate pollution by sewage or some industrial wastes or an intrusion of sea water or other saline water.

- **Fluoride**

While **fluoride** Is considered to be one of the major Ions of sea water, its concentration in sea water, **1.3** mg/kg (Salinity = **35** mg/kg) Is indicative of most natural water concentrations. The guideline value of **(1.5)** mg/1 in drinking water has been proposed by **WHO**.

- **Ammonia**

Ammonia Is formed by the deamination of organic nitrogen - containing compounds and by the hydrolysis of urea. **Ammonia** is readily available as a nutrient for plant uptake and, therefore may contribute greatly to increased biological productivity.

- **Nitrate**

Nitrate, the most highly oxidized form of nitrogen compounds, is commonly present in rural waters, because It is the end produce of the aerobic decomposition of organic nitrogenous matter. Significant sources of **nitrate** are chemical fertilizers from cultivated land, drainage from livestock feed lots, as well as domestic and some industrial waters.

- **Nitrite**

Nitrite is formed in waters by oxidation of ammonium compounds or by reduction of **nitrate**. As an intermediate stage in the nitrogen cycle, it is unstable. Usual concentrations in natural waters are in the range of some tenths of **mg/1**. Higher amounts are present in sewage and industrial wastes, especially in biologically purified effluents, and in polluted streams.

- **Phosphorus**

Phosphate is released into natural waters by the weathering of rocks. Depending on the **pH**, orthophosphate may exist in any of three forms (i.e. $\mathbf{HP0_4^{-2}}$, $\mathbf{H_2P0_4^-}$, $\mathbf{H_3PO_4}$), the predominant forms at **pH 6-8** are $\mathbf{H_2P0_4^-}$ **(10%)** and $\mathbf{HP0_4^{-2}}$ **(90%)**. The latter is the principal nutrient form.

- **Dissolved Oxygen**

The **oxygen dissolved** in surface waters is largely derived from the atmosphere and from the photosynthetic activity of algae and higher aquatic plants. In the surface waters of productive lakes, photosynthesis may produce super saturation by day, and respiration may result in a concentration well below saturation by night. Oxygen is only moderately soluble in water.

- **Selenium**

The chemistry of **selenium** is similar in many respects to that of Sulphur, but **selenium** is a much less common element. The **selenium** concentrations usually found in water are of the order of a few micrograms per liter, but may reach **(50-300)** mg/l in seleniferous areas.

- **Reactive Silica**

Silicon ranks next to oxygen in abundance in the earth's crust. It appears as the oxide (**silica**) in quartz and sand and is combined with metals in the form of many complex silicate minerals, particularly igneous rocks.

- **Sulphate**

Sulphate is an abundant ion in the earth's crust and high concentrations may be present in winter due to leaching of gypsum, sodium Sulphate, and some **shales**. As a result of oxidation of **pyrites**, mine drainage may contain high concentrations of **Sulphate.**

- **Sodium Adsorption Ratio (SAR)**

Excess sodium in irrigation water relative to calcium and magnesium or relative to the total salt content can adversely affect soil structure and reduce the rate at which water moves into and through the soil (infiltration, permeability), as well as reducing the soil aeration. The magnitude of the effect of excess sodium can be related to the relative proportion of sodium ions and calcium plus magnesium ions in the irrigation water. The Sodium Adsorption Ratio (**SAR**) can be calculated as follows:

$$S.A.R. = \frac{Na^{+}}{\sqrt{(Ca^{2+} + Mg^{2+}/2)}}$$

Where concentrations of **Na**$^+$, **Ca**$^{2+}$, and **Mg**$^{2+}$ are expressed in milliequivalents per liter, as totals. When the **SAR** approaches **10**, the probability of soil permeability problems increases.