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Geochemistry

Introduction

Geochemistry is the science or study of the chemistry of the earth. Geochemists those practice this science are interested in the origin of chemical elements, their evolution, the classes and many divisions of minerals and rocks and how they are created and changed by earth processes, and the circulation of chemical elements through all parts of the earth including the atmosphere and biological forms.

Geochemistry is involved many processes; chemical, physical, and biological processes, which lead to distribution and redistribution of the elements through all geologic time.

Geochemistry is the science that uses the tools and principles of chemistry to explain the mechanisms behind major geological systems.

The field of geochemistry extends beyond the Earth, encompassing the whole Solar System, and has made important contributions to the understanding of a number of processes including mantle convection and the origins of rocks. It is an integrated field of chemistry and geology.

Geochemistry is the study of the chemistry of natural earth materials and the chemical processes operating within and on the Earth, both now and in the past.

Geochemistry is fundamentally concerned with the occurrence and distribution of the chemical elements in the Earth, with stronger emphasis on processes occurring in the Earth crust.

The name “Geochemistry” was first used by the Swiss Chemist Schonbein CF in 1838, as earth chemistry.

Goldschmidt (1954), re-defined geochemistry as the study of the distributions and amount of chemical elements in minerals, rocks, soils, water, and the atmosphere, and also the study of the circulation of the chemical elements in nature; on the basis of the properties of their atoms and ions.

Geochemical analyses are carried out on any natural sample such as rocks, volcanic materials, water, soil and sediment. Geochemical analyses involve a wide range of materials and analyses and may be performed for industrial, environmental, or academic reasons.

All of the naturally occurring elements in the periodic table are important for one geochemical investigation or another. Element concentrations may range from major or minor constituents (**>** 0.1%) in one material to trace levels (usually expressed in parts per million) or (parts per billion) in another.

Generally, geochemistry has two branches: **Inorganic Geochemistry** which is the determination of quantity and distribution of individual elements and their inorganic compounds in various parts of the earth (i.e., Atmosphere, Hydrosphere and Lithosphere), and **Organic Geochemistry;** which is the determination of quantity and distribution of organic compounds in various parts of the earth. **Organic Geochemistry** is simply the branch of geochemistry that focuses on organic (carbon bearing) compound found in geologic environments.

The application of geochemistry to geological evaluation (history and reconstruction), economic evaluation (mineral resources, oil and gas exploration) and environmental assessment (pollution studies) is a very powerful tool, when properly applied by those trained in the interpretation of analytical results.

Geochemistry is broadly concerned with the application of chemistry to virtually all aspects of geology, as much as the Earth is composed of the chemical elements, all geologic materials and most geologic processes can be regarded from a chemical point of view.

Some of the major problems that broadly belong to geochemistry are as follows:

1) What is the bulk chemistry of the Earth?
2) What is the chemistry of the major geospheres (from atmosphere to core)

3) To what extent are the elements of the geospheres exchanged?

4) Has the chemical structure evolved over time?

5) The origin and abundance of the elements in the solar system

6) Laws of the distribution and the abundance of elements in the major divisions of the Earth, including the mantle, crust, hydrosphere, and atmosphere

7) The behavior of ions in the structure of crystals

8) The chemical reactions in cooling magmas and the origin and evolution of deeply buried intrusive igneous rocks

9) The chemistry of volcanic igneous rocks and of phenomena closely related to volcanic activity.

10) Origin of ore deposits formed by hot waters derived during the late stages of cooling of magma

11) Chemical reactions involved in weathering of rocks, and The transportation of weathering products in solution by natural waters in the ground and in streams, lakes and the sea.

12) Chemical changes that accompany compaction and cementation of unconsolidated sediments to form sedimentary rocks

13) The progressive chemical and mineralogical changes that take place as rocks undergo metamorphism.

14) Laws that control the movement of elements during geological processes

15) Studying the history of elements and their path, starting with their separation from the magma and the formation of igneous rocks, then the subjection of these rocks to the processes of weathering, transportation, sedimentation, the formation of sedimentary rocks, and then these rocks undergoing metamorphism processes

16) *What are the relations between all the above and life (biogeochemistry)?*

Geochemistry is the study of the chemical processes that form the earth. Geochemistry deals with the abundance, distribution and migration of the chemical elements within the earth.

The simplest term of geochemistry may be defined as the science concerned with the chemistry of the earth as whole and its component parts (Mason, 1966).

Earth is essentially a large mass of crystalline solids that are constantly subject to physical and chemical interaction with a variety of solutions and substances. <u>These interactions allow a multitude of chemical reactions.</u>

Generally geochemistry concerns with the study of the distribution and cycling of elements in Earth's crust. Just as the biochemistry of life is centered on the properties and reaction of **carbon**, the geochemistry of Earth's crust is centered upon **silicon**. Also important to geochemistry is **oxygen**. Oxygen is the most abundant element on Earth. Together, oxygen and silicon account for 74% of Earth's crust.

The eight most common elements found on Earth crust, by weight, are **oxygen** (**O**), **silicon** (**Si**), **aluminum** (**Al**), **iron** (**Fe**), **calcium** (**Ca**), **sodium** (**Na**), **potassium** (**K**), and **magnesium** (**Mg**).

Unlike carbon and biochemical processes where the covalent bond is most common, however, the ionic bond is the most common bond in **Geology**. Rocks are aggregates of minerals and minerals are composed of elements. A mineral has a definite (not unique) formula or composition.

The types of **bonds** in minerals can affect the properties and characteristics of minerals, e.g. **diamonds** and **graphite** are minerals that are polymorphs (many forms) of carbon. Although they are both composed only of carbon, but diamonds and graphite have very different structures and properties.

Pressure and **temperature** affect the structure of minerals. **Olivine**, ($(Fe, Mg)_2$ SiO_4), for example is the only solid that will form at 1,800°C. According to olivine's formula, it must be composed of two atoms of either **Fe** or **Mg**. Olivine is built by the ionic substitution of Fe and Mg, the atoms are interchangeable because they the same electrical charge and are of similar size and thus olivine exists as a range of elemental compositions termed a **solid solution series**. Olivine can thus be said to be "rich" in iron or rich in magnesium.

One goal of geochemistry is the determination of the abundance of the elements in nature. This information is needed to develop hypotheses for the origin of the elements and the structure of the universe.

Subfields of geochemistry

Some subfields of geochemistry are:

A) - Inorganic geochemistry (also called general geochemistry) explains the relationships and cycles of the elements and their distribution throughout the structure of the earth. It provides knowledge about the chemical properties, accumulation and distribution of elements in a variety of rocks and geological environment, as well as the roles of the chemical properties of elements and minerals for geological field.

B) - Exploration geochemistry (also called geochemical prospecting) uses geochemical principles to locate ore bodies, mineral fields, groundwater supplies, and oil and gas fields.

C) - Biogeochemistry is the study of how chemical elements flow through living systems and their physical environments. It investigates the factors that influence cycles of key elements such as carbon, nitrogen and phosphorous.

Biogeochemistry deals chiefly with the cyclic of individual elements and their compounds between living and nonliving systems. Generally biogeochemistry; deals with the behavior of biological materials and their subsequent disposition.

Major problems of biogeochemistry include:

1) The modification of the hydrosphere, and the atmosphere, through the effects of life; and the incorporation of organic materials in rocks.

2) The nature and chemical transformations of biological material present in deposits.

3) Organic chemical reactions influence many geochemical processes.

4) The question of the chemical environment on Earth in which life originated

D) - Sedimentary geochemistry applies chemical principles and techniques to decipher the history of sedimentary rocks from their formation as sediments through lithification to form rocks.

E) - Environmental geochemistry is the newest branch of the geochemistry and came into prominence in the 1980s. Environmental geochemistry concerns with the sources, distribution and interactions of chemical elements in organic tissues, groundwater, surface water, marine environment, soil, and rocks.

F) - Hydrogeochemistry involves the chemistry of ground and surface waters, particularly the relationship between the chemical characteristics and quality of waters and regional geology.

Hydrogeochemistry explains the role of water in the migration and redistribution of chemical elements in the Earth's crust. The most important topics of this branch is the study of the origin of water and its chemical composition, the type of chemical elements in it and the study of the processes that take place between water and sediments.

G) - Cosmochemistry includes the analysis and the distribution of elements in the cosmos.

Cosmochemistry is the chemical analysis of extraterrestrial materials. Cosmochemical studies are useful in verifying information about the origin and development of the Earth, the formation of its layers, and the evolution of geological processes during the history of the Earth.

H) - Isotope geochemistry involves the determination of the relative and absolute concentrations of the elements and their isotopes in the Earth and on Earth's surface. **There are two main divisions** of isotope geochemistry, namely stable isotope geochemistry (non-radioactive) and isotope geochemistry of radioactive origin.

Geochemical Analysis

Geochemical analysis is the process through which scientists determine the chemical compounds that constitute Earth. To a lesser degree, geochemical analysis can also be used to understand extraterrestrial materials such as moon rocks or Martian soil samples.

The process or geochemical analysis requires a thorough grounding in chemistry and Earth sciences, as well as an understanding of the different ways in which elements can interact in a given geologic situation.

Geochemical analysis can be used to help predict where petroleum, metals, water, and valuable minerals.

Geochemical analysis became important in the nineteenth and twentieth centuries, when chemists first began investigating the compounds that formed naturally in the earth, air, and water. Much of this early work was credited to a chemist named **V. M. Goldschmidt**, who with his students created detailed charts of the chemical breakdown of common compounds, mainly igneous rocks.

Goldschmidt also created a series of guidelines known as **Goldschmidt's rules** for understanding the different ways in which elements interact to form different types of rocks. Goldschmidt based his analysis of chemical behavior on two separate items: **size** and **electrical** charge.

Scientists have expanded on Goldschmidt's program, forming a series of disciplines that help them predict and interpret the chemical composition through time of this planet, other objects in the solar system (including planets), and their constituent ingredients.

Later, scientists have added radiation to the process of geochemical analysis, grouping elements by their radioactive and stable isotopes. Isotopic analysis can give clues to the place of origin of the compound and the environment in which it was first put together. Isotopes are also used to determine the age of a compound and the study of the process through which they decay from one form to another is known as geochronology.

Branches of geochemical analysis

A number of different analytical techniques for the analysis for inorganic geochemical materials are used within the laboratory, e.g. X-ray Fluorescence (**XRF**) Spectrometry, Inductively Coupled Plasma Mass Spectrometry (**ICP-MS**), the electron probe micro-analyzer (**EPMA**), and Scanning Electron Microscope (**SEM**)

The **XRF** is used for analysing fusion and pressed powder samples for elements. The equipment can measure concentrations as low as 1 ppm and as high as 100%.

The electron probe micro-analyzer (**EPMA**) can be used for the analysis of elements in very small areas such as individual mineral crystal or grains.

Scanning Electron Microscope (**SEM**) has been reported to be useful in sample imaging by scanning with high energy beam of electrons. It is termed a useful tool for photonics research based on Nano-scale surface.

Behaviour of elements in the geological environment

The most important aspects of the behaviour of chemical elements in the geological environment are their **mobility**, their **compatibility**, and their **ability to substitute into** the crystal structure of a mineral. These educe directly from the element characteristics, specifically **ionic size** and **charge**, and the physical and chemical conditions of the relevant processes.

Mobility

The mobility of a chemical element in the geological environment, and specifically during **metamorphism**, **alteration,** and **weathering** processes (i.e., in presence of free water) is conditioned by its ionic potential. Elements tend to fall in one of the following categories:

Mobile cations: They **don't form strong** bonds with O^{2-} and quickly break from it. As a result, they will move as dissociated ions in aqueous solution, such as K^{1+}, Na^{1+}, Ca^{2+}, Pb^{2+}, and so on.

Immobile ions: Because of their higher ionic charge, they provide a more focused charge that **forms strong bonds** with $\mathbf{O^{2-}}$ in solids. Thus they will tend to be immobile during metamorphism and alteration. However, these elements may become somewhat mobile at very high water-to-rock ratios.

Mobile oxyanions; these elements have the highest ionic charge, which allows them to **form very strong bonds** with **O^{2-}** (or other ligands). Accordingly, these elements will be mobile by associating to oxygen, or other ligands such as BO^{3-}, CO^{2-}, PO^{3-}, SO^{2-}, and so on.

Generally, there are many factors controlling the mobility:

a) The elements' own characteristics

b) The **availability of oxygen**, or the oxidation–reduction potential (**Eh**) of the system, which will control the valance state of the elements. Let us take **Fe** as an example: as **Fe^{2+}** it is mobile in **reducing** environment (low Eh), whereas it is immobile as **Fe^{3+}** in oxidizing environment (high Eh). **Uranium** is the exact opposite: it is **immobile** as **U^{4+}** at low Eh where it forms minerals such as uraninite (UO_2), and is **mobile** as **U^{6+}** under oxidizing conditions where it moves as various uranyl complexes, such as $UO_2(HPO_4)_2^{2-}$ or $UO_2(CO_3)^{2-}$

c) The **availability of other ligands** than O, such as Cl, F, or organic acids in the system

d) The **availability of water**.

e) Temperature: as a general rule, mobility increases with higher temperature.

Compatibility

Another very important consideration of the behaviour of elements in the geological environment is the compatibility of an element with the silicate crystalline structure.

During any igneous process where there is co-existence of a silicate melt and **Fe–Mg** silicate crystalline structure, an element will preferentially partition into the crystalline phase (compatible) or into the liquid phase (incompatible).

Compatibility is a term used by geochemists to describe how elements partition themselves in the solid phase and silicate melt.

During fractional crystallization the most mafic minerals will crystallize first, predominantly Mg - Fe silicates. According to Bowen's Reaction Series, the most compatible elements will tend to partition preferentially into the solid phase leaving the liquid phase enriched in incompatible minerals. Inversely, during partial melting the most incompatible elements will tend to leave the silicate crystalline structure and partition preferentially into the silicate melt.

In geochemistry, **compatibility** is a measure of how trace element substitutes for a major element within a mineral.

Compatibility is not an absolute quantifiable value, but rather a ***relative quality***. At any given point during co-existence of a silicate melt and silicate minerals, the ***more compatible*** elements will tend to partition into the minerals and the ***more incompatible*** will tend to partition into the liquid phase.

Generally **compatibility** controls the partitioning of different elements during the crystallization of silicate melt.

Compatibility of an ion is **controlled by two things**: its valence and its ionic radius. e.g. (olivine) has the chemical formula $(Mg,Fe)_2SiO_4$, **Nickel** with similar chemical behaviour to **iron** and **magnesium**, so it substitutes readily for them and hence is very compatible in olivine.

The important observation that the more mafic and less differentiated rocks are more enriched in compatible elements: and inversely, more differentiated and more felsic rocks are more enriched in incompatible elements.

In general, **incompatible** elements are enriched in the continental crust and depleted in the mantle. Examples include: rubidium, barium, uranium, and lanthanum.

Compatible elements are depleted in the crust and enriched in the mantle, with examples nickel and titanium

Substitution

The concept of compatibility is to a certain extent, related to and conditioned by the possibility of element substitutions in a mineral crystal structure. The mineral crystal structure is relatively rigid and can distort only to a limited extent, which means that the size of the ions is a factor. A mineral also has to be electrically neutral, this meaning that the charge of an ion will also be a factor.

According to the Goldschmidt's rules, substitutions are affected by the ionic size, ionic charge, ionic potential, and electronegativity.

Substitutions are also affected by the physical and chemical conditions of the system. Higher temperature will allow for higher substitution possibility, because of the thermal expansion of minerals, creating space for larger ions. Inversely, higher pressure will result in lower possibility for substitutions, because of increasing pressure causes compression.

Finally, the availability of ions in the system also has a direct effect on substitutions and controls to a significant degree the extent of substitutions that occur during any given geological process.

Geochemical classification of elements

There are many ways to group the chemical elements in separate categories. We can use a particular characteristic (e.g., size, weight), or their place in the periodic table of the elements, or their belonging in a particular reservoir, or their behaviour. The simplest way would be to separate the chemical elements into ***metals***, ***non-metals***, and ***gases***. This classification of the elements is very common, and we will rely on it and use it extensively, but it is not specific to geology and is not particularly helpful from the point of view of the geological environment and processes. For our purposes in geochemistry, we have to consider some other factors, relevant to geology, abundance on Earth and where they are most likely to be found and behaviour and distribution of the elements in the Earth.

Generally, elements are simply classified:

1- **Based on abundances**
2- **Based on behaviour and distribution of elements in the Earth** (*Goldschmidt classification*)

1 - Classification of elements based on abundances

For any practical purpose, this is the most important classification. We will separate the elements in the groups of

major and **trace** elements. Elements are divided according to their abundance into two groups:

A)- Major elements

Major elements (**Si, O, Al, Mg, Fe, Ca, Na, K, Mn and Ti**): these are the main constituents of a rock and are very likely to be present in concentrations above 0.1 wt%. Their concentrations are reported as weight percent of oxides (wt%). The oxides of the major elements account for approximately 99 wt% of the elements present in rocks on the continents

Geochemistry of major elements have been done by X-ray fluorescence (XRF)

B) Trace elements

Trace elements are those which occur in very low concentrations in common rocks (usually < 0.1 % by weight). Their concentrations are commonly expressed in parts per million.

Unlike major elements, trace elements tend to concentrate in fewer minerals, and are therefore more useful in formulating models for magmatic differentiation, and in some cases, in predicting the source of a particular magma.

Trace elements most commonly used for the interpretation of the petrogenesis of igneous rocks include: **Ni, Cr, Sc, V, Rb, Ba, Sr, Zr, Y, Nb and the rare earth elements.**

Keep in mind that the concentration of trace elements will vary with the rock type; whereas **Ni** and **Cr** show higher concentrations in mafic and ultramafic rocks, but **Zr** and **Rb** are more concentrated in acidic rocks.

The incorporation of a trace element in the crystal structure of minerals depends largely on its charge and radius, also on the electronegativity of this element. Accordingly, a trace element will either substitute for a major element in the structure of a crystallizing mineral, or remain in the liquid. **Trace elements are simply classified into compatible and incompatible elements**

A. Compatible elements

The concentration of compatible elements is abundant in Fe-Mg minerals (especially olivine) which separate early from the magma.

The group of compatible elements includes: nickel, cobalt, chromite, vanadium and scandium (Ni, Co, Cr, V, Sc). They are the elements whose concentrations increase in Fe- Mg minerals, which separate early from the magma, due to the conformity of their properties with the crystal structure of those minerals.

B. Incompatible elements

Incompatible elements can not enter the crystal structure of Fe- Mg minerals, which separate early from the magma, so they tend to concentrate in the liquid phase during the fractional crystallization process

In addition to this simple classification of trace elements into **compatibles** and **incompatibles**, trace elements are perhaps better classified on the basis of their geochemical characteristics into:-

I- Large-ion lithophile elements (LILE)

These elements are characterized by large ionic radii, and low charges, and will therefore preferentially concentrate in the liquid until a particular phase with large enough sites to accommodate them begins to crystallize. These elements will be incompatible, particularly with respect to mantle phases (Ol, Opx, Cpx,). Examples include: Rb, Sr, Cs and Ba.

II- High field strength elements (HFSE)

These are elements which have large cations, and also large charges, and are also excluded from mantle phases and more concentrated in residual liquids (i.e. they will be largely incompatible).

These elements are concentrated in accessory phases as sphene, zircon, and apatite. Examples include Zr, Hf, Nb, Ta, Th and U.

III- Transition elements

These elements are characterized by relatively small ionic radii, and are either bi- or tri-valent.

These elements are strongly accommodated in the solid phases that crystallize during the early stages of magmatic evolution, and are therefore "compatible" with mantle phases (Ol, Opx, Cpx,). Examples include Ni, Co, Cr, and Sc.

IV- Rare earth elements (REE)

This is a group of elements with atomic numbers between 57 (La) and 72 (Lu) characterized by relatively large ionic radii, and valences of either $^{+}2$ or $^{+}3$.

However these elements occur in very low concentrations in igneous rocks, they are very important for petrogenetic interpretations.

2 - Classification of the elements based on behaviour and distribution in the Earth (Goldschmidt classification)

Because of their specific characteristics and behaviour, the chemical elements tend to concentrate in specific Earth reservoirs. Many of them belong to more than one reservoir, and the chemical elements are divided into four groups

The best-known geochemical classifications of the elements were put forth by the Norwegian geochemist V. M. **Goldschmidt** (1924).

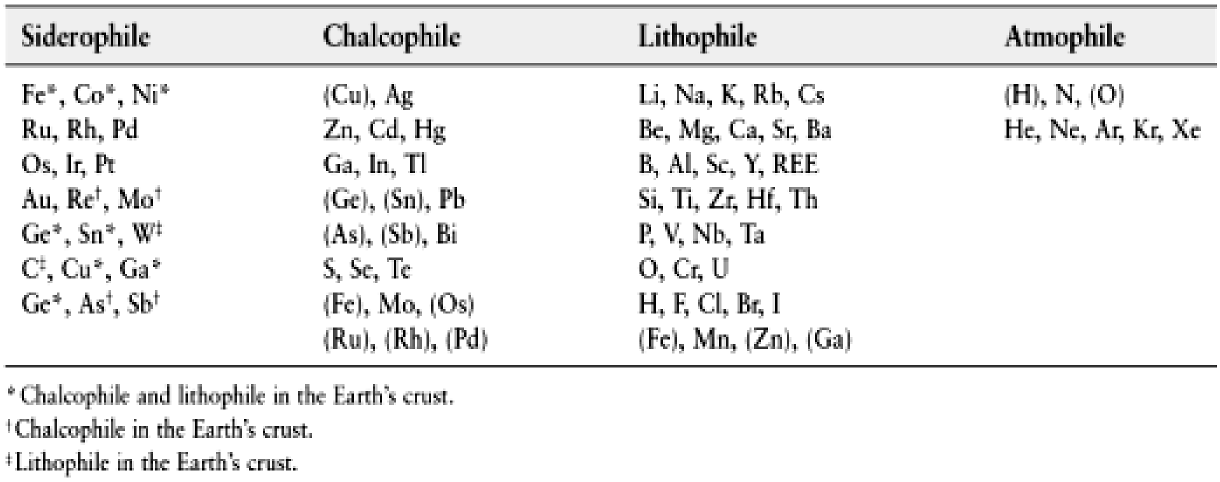
Goldschmidt was the first to point out the importance of this primary geochemical differentiation of the elements. In Goldschmidt's classification the **chemical elements are divided into four groups** taking into account the positions of the elements in the periodic system, the types of electronic structures of atoms and ions, and the specifics of the appearance of an affinity for a particular anion.

How classified elements based on distribution in the Earth? (Goldschmidt classification)

The **Goldschmidt classification**, is a geochemical classification which groups the chemical elements according to their preferred host phases into **lithophile** (rock-loving), **siderophile** (iron-loving), **chalcophile** (ore-loving), and **atmophile** (gas-loving) or volatiles

For example *lithophile* element, such as potassium, will be in highest concentration in the magma rich in silica; whereas a *siderophile* element, such as platinum, palladium ; will be most enriched in the Fe-Ni melt.

Table: 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.

Figure 1: Goldschmidt’s classification of the elements

Lithophile element

Lithophile elements are those that remain on or close to the surface because they combine readily with oxygen, forming compounds that do not sink into the core.

The lithophile elements such as: Si, K, Al, Mg, Ca, Na, Ti, Ba, Cr, F, Sr, Ta, Li, Nb, Rb , V, Y, Zr.

Lithophile elements mainly consist of the highly reactive metals and also include a small number of reactive nonmetals.

Lithophile derives from "lithos" which means "rock", and "phile" which means "love".

Most lithophile elements form extremely ionic bonds. Their strong affinity for oxygen causes lithophile elements to associate very strongly with silica, forming relatively low-density minerals that thus float to the crust.

The more soluble minerals formed by the alkali metals tend to concentrate in seawater or extremely arid regions. The less soluble lithophile elements are concentrated on continental shields

Because of their strong affinity for oxygen, most lithophile elements are enriched in the Earth's crust. The nonmetallic lithophiles – phosphorus and the halogens exist on Earth as ionic salts seawater.

Several transition metals, including **chromium**, **molybdenum**, **iron** and **manganese**, show *both* **lithophile** *and* **siderophile** characteristics and can be found in both these two layers.

Siderophile elements

Siderophile (from *sideron*, "iron", and *philia*, "love") elements are the high-density metals which tend to sink towards the core because they dissolve readily in iron either as solid solutions or in the molten state.

The **siderophile elements** include cobalt, iron, iridium, manganese, molybdenum, nickel, osmium, palladium, platinum, rhenium, rhodium and ruthenium.

Most siderophile elements have **no affinity** for oxygen. Thus, siderophile elements are bound through **metallic**

bonds with iron in the dense layer of the Earth, where pressures may be high enough to keep the iron solid.

Because they are so concentrated in the dense core, siderophile elements are known for their rarity in the Earth's crust. Most of them have always been known as precious metals. Iridium is the rarest transition metal occurring within the Earth's crust, with abundance by mass of less than one part per billion.

Chalcophile elements

The chalcophile elements include: Ag, As, Bi, Cd, Cu, Ga, Ge, Hg, In, Pb, Po, S, Sb, Se, Sn, Te, Tl and Zn.

Chalcophile elements are those that remain on or close to the surface because they combine readily with sulfur rather than oxygen, forming compounds which do not sink into the core.

Chalcophile elements are those metals have a low affinity for oxygen and **prefer to bond with sulfur** as highly insoluble sulfides.

Chalcophile derives from Greek meaning "ore". Because these sulfides are much denser than the silicate minerals formed by lithophile elements, chalcophile elements separated below the lithophiles at the time of the first crystallisation of the Earth's crust. This has led to their depletion in the Earth's crust relative to their solar abundances.

Some chalcophile elements like Zinc and gallium are somewhat "lithophile" in nature because they often occur in silicate or related minerals and form quite strong bonds with oxygen. Gallium, notably, is sourced mainly from bauxite, an aluminum hydroxide ore in which gallium ion substitutes for chemically similar aluminum.

Although no chalcophile element is of high abundance in the Earth's crust, chalcophile elements constitute the bulk of commercially important metals. This is because, whereas lithophile elements require energy-intensive electrolysis for extraction, chalcophiles can be easily extracted by reduction with coke.

Atmophile elements

The atmophile elements are: H, C, N and the noble gases. Atmophile elements (also called "volatile elements") are defined as those that remain mostly on or above the surface because they are occur in liquids and gases at temperatures and pressures found on the surface.

Hydrogen, which occurs in the water, is also classed as an atmophile. Water is classified as a volatile, because most of it is liquid or gas, even though it does exist as a solid compound on the surface.

Carbon is also classed as an atmophile because it forms very strong multiple bonds with oxygen in carbon monoxide and carbon dioxide. The latter is the fourth-largest constituent of the Earth's atmosphere, while carbon monoxide occurs naturally in volcanoes.

Because all atmophile elements are either gases or form volatile hydrides, atmophile elements are *strongly depleted* on earth.

Summery of Goldschmidt classification

1. Lithophile elements show an affinity for silicate phases and are concentrated in the silicate portion (**crust**) of the Earth. They have a high bonding affinity with oxygen.

Lithophiles have an affinity to form ionic bonds and are represented by silicates (silicon and oxygen) in the crust.

2. Siderophile elements exhibit a weak affinity to both oxygen and sulphur and exhibit an affinity to form metallic bonds. They are depleted in the silicate portion of the earth crust and concentrated in the core.

3. Chalcophile elements have an affinity for a sulphide phase. They have a bonding affinity usually in the form of covalent bonds with sulfur.

4. Atmophile elements are generally extremely volatile and are concentrated in the atmosphere and hydrosphere and characterized by their ability to form van der Waals bonds.

5. Goldschmidt was aware that many elements can occur in two or more valence states and when they do, they may exhibit different affinities. For example, in reducing environments, $\mathbf{Cr^{3+}}$ is strongly *chalcophile*; whereas under oxidizing conditions, $\mathbf{Cr^{6+}}$ is distinctly *lithophile*.

Another example is that **phosphorus** has an affinity for iron metal in the reduced form and in the oxidized form it has *lithophile* character and occurs as phosphates in crustal rocks. Different valence forms of the same element can behave chemically as differently as different elements.

Geochemical characteristics of the Earth's interior

The interpretation of seismic data provides a primary threefold division of the earth into crust, mantle and core (Fig.2), together with other geophysical evidence; these data also give some indication of the physical properties of the material making up the three parts.

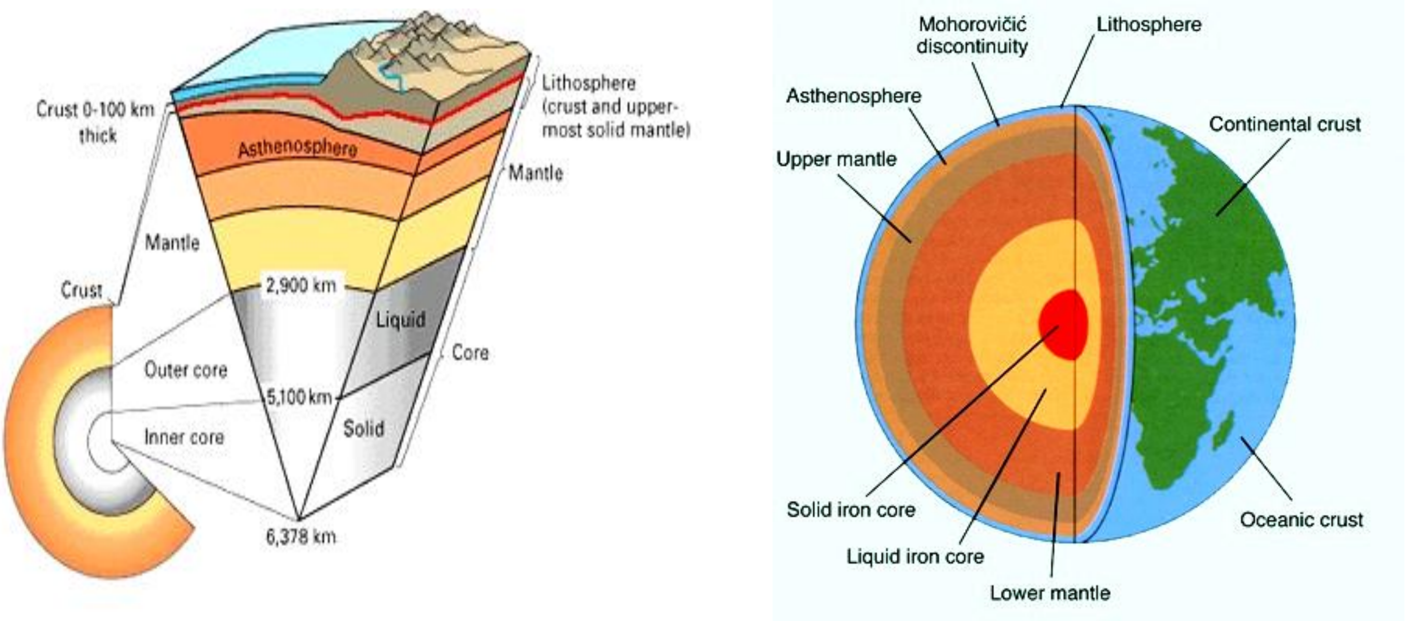


Figure 2 : The internal structure of the Earth

The crust is directly accessible to our observations. It is heterogeneous and varies in thickness from place to place.

The earth's crust is a thin skin which covers the whole surface but forms only 0.2% of the total mass of the earth.

Marked differences exist between the continents and oceanic crust. Deep ocean basin is between 10 and 13 km below sea level, however the continents crust is usually about 40 km.

The crust is the outermost layer of rocks making up the solid Earth. It is distinguished from the underlying mantle rocks by its composition, lower density, and the lower velocity at which it conducts seismic energy.

Most of the crust can be classified either as **'continental'** or **'oceanic'**. These two types of crust differ in their average age, composition, thickness and mode of origin.

Continental crust

Continental crust is on average older, rich in silica and thicker than oceanic crust, but is also more variable in each of these respects.

The oldest parts of the continental crust, known as 'shields' or 'cratons', include some rocks that are nearly 4billion years old.

Most of the continental crust consists of the roots of mountain belts, known as 'orogens', formed at different stages in Earth history. Over large areas, however, these orogens are covered by younger sedimentary rocks.

New continental crust is still being generated by processes operating at subduction zones. However, sediments eroded from the continental crust and deposited on the ocean floor are also recycled into the mantle at some subduction zones.

The average thickness of the continental crust is about 40 km, but beneath parts of the Andes and the Himalaya mountain ranges the crust is more than 70 km thick.

The seismic evidence on the **continental crust** indicates two principal layers; an upper one of granitic to granodiorite composition and a lower of basaltic composition. Theses two layers correspond to the ***sial*** (i.e. material rich in **Si** and **Al**) and ***sima*** (rich in **Si** and **Mg**), respectively.

The continental crust is a mosaic of sediments, metamorphosed sediments, igneous intrusions of different kinds and volcanics, and there is probably a gradual change in the average composition of the material from the surface farther down.

Oceanic crust

Oceanic crust underlies most of the two-thirds of the Earth’s surface which is covered by the oceans. It has a remarkably uniform composition. Oceanic crust is very thin (less than 10km thick) and dense and is composed largely of basic igneous rocks covered by a thin layer of deep-sea sediments. New oceanic crust is constantly being generated by sea-floor spreading at mid-ocean ridges, while other parts of the oceanic crust are being recycled into the mantle at subduction zones.

The chemical composition of the Earth's crust

What is the composition of the Earth's crust?

Although it is unlikely that we will be able to visit the Earth's deep interior any time soon, we can still resolve chemical and mineralogical changes on the basis of seismic wave behavior.

Volcanoes also give us some idea of the materials that compose the Earth's interior.

So what exactly is the composition of the Earth's interior? It depends upon the depth that you are interested in. The crust is different than the mantle and the mantle is different than the core. Since we live on the crust, it is perhaps best to focus on crust rather than others.

There are two general types of crust:-

1) Continental crust **2**) Oceanic crust

The average composition of the crust is in effect that of igneous rocks, since the total amount of sedimentary and metamorphic rocks is insignificant in comparison to the bulk of the igneous rocks, and in any case their average composition is not greatly different.

Clarke and Washington (1924) estimate that the upper 10 miles of the crust consist of **>** 90% igneous rocks, where sedimentary rocks are present; they form relatively thin layers on an igneous basement, except where locally thickened in orogenic belts.

Clarke and Washington estimate of the average composition of igneous rocks, which is sometimes used as the average composition of the crust. The overall of the 5159 analyses as following:

SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
60.18	15.61	3.14	3.88	3.56	5.17	3.91	3.19	1.06	0.30

Polder vaart (1955) analyzed the composition of the crust in terms of four major geological divisions - the deep oceanic region, the continental shields, the young folded belts, and the continental platform and slops. For each of these divisions he has an average composition. From these data he finally arrived at an average composition for the crust, this average as following:

SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
55.2	15.3	2.8	5.8	0.2	5.2	8.8	2.9	1.9	1.6	0.3

Goldschmidt pointed out the earth's crust consist almost entirely of oxygen compounds, especially silicates of Aluminum, Magnesium Sodium, Potassium and Iron. The following table lists the 8 most common elements (in weight percent) of average crust:

Element	Oxygen	Silicon	Aluminum	Iron	Calcium	Sodium	Potassium	Magnesium	other elements
Wt%	46.6	27.7	8.1	5.0	3.6	2.8	2.6	2.1	1.5

Thus the crust of the earth is essentially a packing of oxygen anions, bonded by silicon and the ions of the common metals.

The mantle

The geophysical data indicate that the **mantle** has a layered structure. It's possible to differentiate the mantle into several chemically distinct layers (Fig.2). The chemical composition of the mantle varies between its layers. Overall, the normalized composition of the mantle is estimated to be similar to that of the ultramafic rock peridotite (which is composed of olivine, clinopyroxene, orthopyroxene).

Between about 400 km and 650 km depth, olivine is not stable and is replaced by high pressure polymorphs **spinel** mineral types ($MgAl_2O_4$).

Below about 650 km, all of the minerals of the upper mantle begin to become unstable and the most abundant minerals are perovskites. The **Perovskite** minerals are a group of oxides with a general formula of **AXO_3 (***calcium titanium oxide ($CaTiO_3$)***)**. The **A** can be either calcium, strontium, lead and/or various rare earth metals. The **X** site can be occupied by titanium, and/or iron.

Perovskite may form up to 90% of the lower mantle, followed by the magnesium / iron oxide **ferropericlase** {*magnesium / iron oxide (Mg,Fe)O*}. The changes in mineralogy at about 400 and 650 km yield distinctive signatures in seismic records of the Earth's interior, and like the **Moho**, are readily detected using seismic waves.

The mantle differs in its chemical ratios from the crust; however it is composed of roughly : 45% oxygen, 23% magnesium, 22% silicon, 6% iron, 2% aluminum, 2% calcium, with trace amounts of sodium, potassium, and other elements (Table 3).

Table 3: Composition of Earth's mantle in weight percent

Element	Amount		Compound	Amount
O	44.8			
Si	21.5		**SiO_2**	46
Mg	22.8		**MgO**	37.8
Fe	5.8		**FeO**	7.5
Al	2.2		**Al_2O_3**	4.2
Ca	2.3		**CaO**	3.2
Na	0.3		**Na_2O**	0.4
K	0.03		**K_2O**	0.04

The mantle is divided into an **upper** mantle and **lower**, which are separated by a **transition zone**. Even further breakdowns can follow:

Upper mantle (to 400 km) - The upper mantle is composed of solid ultramafic rocks, high in olivine and pyroxene content. The boundary of the upper mantle with the crust is marked by the "Moho" discontinuity, here seismic waves refract when passing across the boundary due to the differing compositions of the crust and mantle

Subducted crust is assimilated into the upper mantle, often at the expense of felsic minerals, which are fractionally melted and form volcanoes.

The upper part of this region interacts closely with the crust. The topmost 50-120 km (depth varies regionally) of the upper mantle is considered part of the ***lithosphere*** (the solid portion of the Earth. It includes the crust and the part of the upper of mantle), below this lies the ***asthenosphere***, a region where the mantle is partially-melted and behaves plastically. This region is thought to be the source of mafic (basaltic) magmas.

Mesosphere (400-1000 km) - This is the transition zone between the upper and lower mantle. Here, the pressure from overlying rock is sufficient to overcome the temperature gradient, making the mesosphere less susceptible to deformation.

Chemically, the mesosphere is higher in calcium and aluminum.

Lower mantle (1000-2900 km) - The lower mantle is separated from the transition zone by another seismic discontinuity, this one as with the Moho, marks a compositional change between layers.

The lower mantle is richer in Iron and Nickel. At the base of the lower mantle is a poorly-understood layer marked by yet another discontinuity, this may be an iron-rich zone of transition between the outer core and mantle.

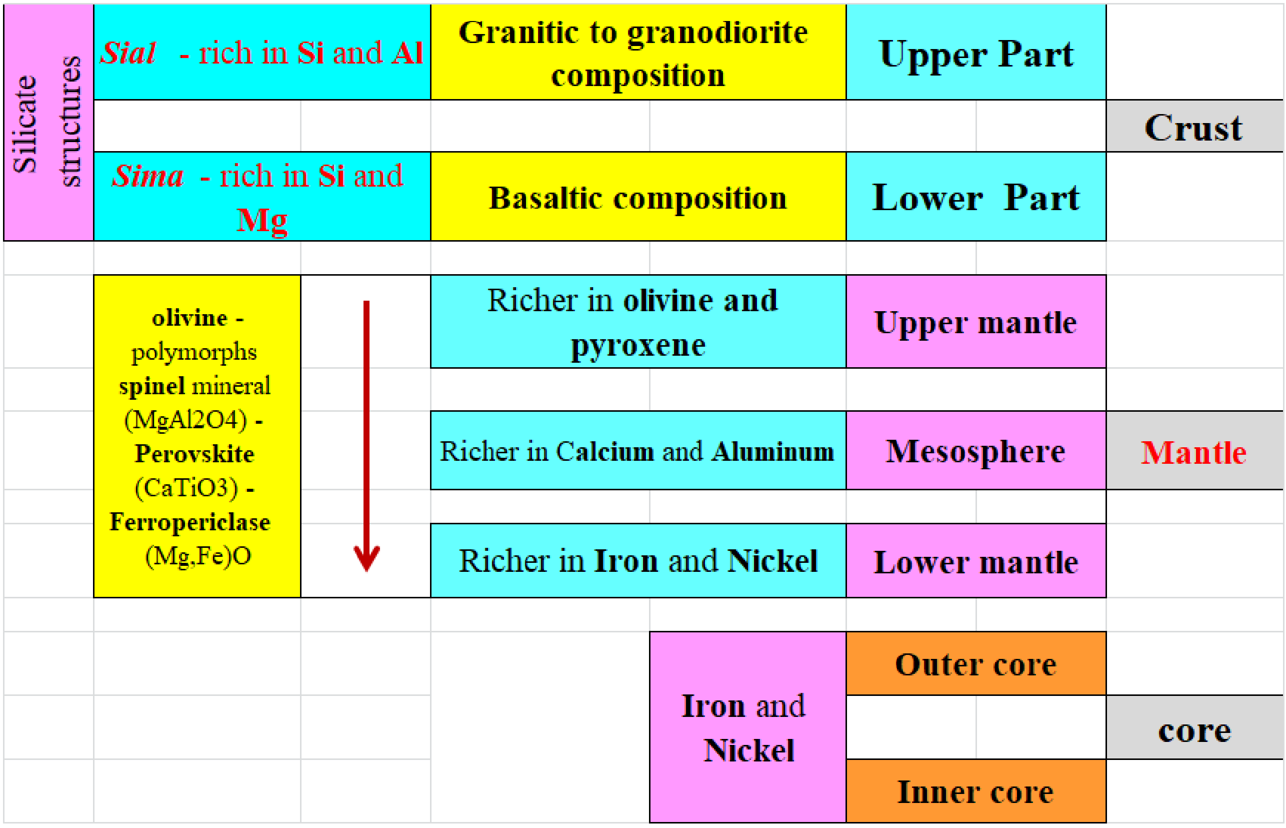
The core

The composition of the Earth's core is fundamentally resolved by combining observations from geophysics, cosmochemistry and mantle geochemistry. The core is divided into two parts, a solid inner core with a radius of ~1250 km and a liquid outer core extending beyond it to a radius of ~3500 km. The inner core is generally believed to be solid and composed primarily of iron and some nickel. The outer core surrounds the inner core and is believed to be composed of liquid iron mixed with liquid nickel and trace amounts of lighter elements.

Inner Core is the central part of the iron-nickel core, which is a solid iron sphere. The reason that the iron is solid is that the pressure at the center of the Earth is significantly higher than the pressure above, while the temperature is only slightly higher. While higher temperature would tend to melt materials, higher pressures tend to create solids.

Outer Core constitutes the remainder of the iron-nickel core and is liquid. It is liquid because the pressure is lower.

Chemical characters of Earth's interior



Silicate structures	*Sial* - rich in **Si** and **Al**		**Granitic to granodiorite composition**	**Upper Part**	**Crust**
	Sima - rich in **Si** and **Mg**		**Basaltic composition**	**Lower Part**	
	olivine - polymorphs **spinel** mineral ($MgAl_2O_4$) - **Perovskite** ($CaTiO_3$) - **Ferropericlase** (Mg,Fe)O	↓	Richer in **olivine and pyroxene**	**Upper mantle**	**Mantle**
			Richer in **Calcium** and **Aluminum**	**Mesosphere**	
			Richer in **Iron** and **Nickel**	**Lower mantle**	
			Iron and **Nickel**	**Outer core**	**core**
				Inner core	

Geochemical distribution of elements

The science of geochemistry is concerned with the determination of the relative and absolute abundance of the elements in the earth and the study of the distribution and migration of the individual elements in the various parts of the earth. With the object of discovering the principles governing this distribution and migration

Each rock may be regarded as a chemical system in which, chemical changes may be brought about. Every such change implies a disturbance of elements, equilibrium, with the formation of a new system, and is itself stable under the new conditions. (Clark 1924)

1)-Behaviour of major elements in igneous systems (*During magmatic crystallization*)

Most igneous rocks are formed by the differentiation of basaltic magma, mafic minerals, settling out first to form ultramafic rocks and the remaining melt changing in composition through the series gabbro-diorite-granodirite-granite-pegmatite, so we can say "***early formed minerals***" of high melting point, such as olivine and calcic plagioclase, "***late- formed minerals***" like quartz and biotite, and ***"residual fluids***" of pegmatitic composition. ***We can work out some rules of behavior for various elements during such a differentiation process***

Behavior of major elements during differentiation process discuss as:

(A) Rules of the distribution

(B) Regularities of distribution

A)-Rules of the distribution

A-1: Overview

For an element to crystallize in a mineral of its own a mineral in which it is a major constituent requires that the element be present in the melt in appreciable amounts. If only a few ions of the element are present, they can be taken up by the crystal structures of the major silicates, either as replacements of an abundant element or as random inclusions in the crystal lattice.

The sequence minerals that separate during differentiation of a silicate melt, are commonly olivine and calcic plagioclase appear first; as the temperature falls, part or all of the olivine reacts with the melt to form pyroxene, then amphibole, then biotite; the composition of the plagioclase meanwhile becomes increasingly sodic; near the end of the crystallization, quartz and potash feldspar appear along with sodic plagioclase.

What are the possible variations of major elements during differentiation process?

The possible variations of major elements during differentiation are:-

1) Most of the magnesium and calcium leave the melt in early stages of differentiation

2) Most of the alkali metals leave the melt later

3) Iron may be largely concentrated in early minerals or may appear at all stages of differentiation

4) Aluminum drops out in feldspars during the differentiation process, and also in micas toward the end.

5) The trace elements can be accommodated in the silicate structures of major elements depend **on the characteristics** of its ions, **for example:**-

   a) **Rubidium** is so similar to **Potassium,** so it can be accommodated as replacements (Rb^+ for k^+) in micas and feldspars.

   b) **Zirconium** cannot fit easily into common silicate structures, and it goes into separate crystals of the accessory mineral zircon.

   c) **Copper** is not capable of forming its own minerals or substituting common ions in silicate structures, so is concentrated in the residuals solution.

A-2: The rules of replacement

Outlined the rules of replacement of elements in silicate structures?

The specific characteristics of an element, determine which way it will behave. Generally the rules of replacement as the following:-

1) A trace element may substitute extensively for a major element if the ionic radius does not differ by more than about 15%.

2) Ions whose charges differ by one unit may substitute readily for one another. Substitution is generally slight when the charge difference is more than one unit

3) If two ions have the similar radii and similar charges, the smaller ion will be concentrated in early fractions of mineral (will enter a crystal structure firstly).

يسبق ايون المغنسيوم Mg^{2+} (0.66 انجستروم) ايون الحدبدوز Fe^{2+} (0.74 انجستروم) فى دخول جميع المعادن الحديدومعنيسية مثل الاولفين والبيروكسين

4) If two ions have the similar radii but different charges, the ion with the higher charge will enter a crystal structure preferentially (firstly).

يسبق ايون الكالسيوم Ca^{2+} ايون الصوديوم Na^{+} فى دخول البناء البلورى لمعادن البلاجيوكليز وذلك بسب شحنته الاعلى.

5) Of two ions that can occupy the same position in a crystal structure, the ion with the smaller radius or the higher charge forms the stronger bonds with its neighbors, and will enter a crystal structure firstly.

6) When a trace element has the same charge and an ionic radius similar to a major element, we speak of it as **camouflaged** in the crystal lattice containing the major element. Thus Hf $^{4+}$ (0.78 A) is camouflaged in zirconium (Zr^{4+} 0.79 A) minerals

7) When a trace element has a similar ionic radius but a higher charge than that of a major element (or the same charge but a lesser radius), we speak of it as **captured** by the crystal lattice containing the major element. Thus Ba^{2+} (1.34 A) is captured by potassium minerals (K^{+} =1.33 A).

8) When a trace element has a similar ionic radius but a lower charge than that of a major element (or the same charge but a greater radius), we speak of it as **admitted** by the crystal lattice containing the major element. Thus Li^{+} (0.68 A) is admitted into magnesium (Mg^{2+} = 0.66 A) minerals.

From the upper points, we could predict the following:-

- **a.** According to rule No.2 , Ba^{2+} (1.34 A) would commonly substitute for K^{+} (1.33 A), also Cr^{3+} substitute for Fe^{3+}
- **b.** In an isomorphous pair of compounds, the one containing ions of higher charge would have the higher melting point (because of the stronger bonding) and therefore would appear earlier in a crystallization sequence.

c. According the similarity in ionic radii; trace element like **Li^+**, which substitutes extensively for **Mg^{2+}** because of the similarity in their ionic radii, and it should be concentrated in late-forming **Mg** minerals rather than early ones because its single charge forms weaker bonds than the double charge on **Mg^{2+}** ; so the absence of **Li^+** in olivine and its common presence as a substitute for **Mg^{2+}** in the micas of pegmatites.

d. (According the similarity in ionic radii) Rb^+ (1.47 A), having an ion similar in charge to K^+ (1.33 A) but somewhat larger, so it should be enriched in late K minerals rather than early ones, and it should be concentrated in the micas of pegmatites.

e. Sr^{2+} (1.12 A), with a radius between those of ca^{2+} and K^+, and can substitute for both

f. In the series of the olivines, **foresterite** is enriched in early crystals than **fayalite**, corresponding with the fact that **Mg^{2+}** is a smaller ion than **Fe^{2+}**.

Sometimes the rules of substitution according to ionic radius are less satisfactory, for example**:-**

1) **Cu^+** (copper ion) is similar in size and charge to **Na^+**, but copper doesn't show any enrichment in sodium minerals.

2) Cadmium ion (**Cd^{2+}**) closely resembles calcium ion (**Ca^{2+}**) in size and charge but is not concentrated in calcium minerals.

The above difficulties are due to:-

- The difference in **bond character**
- The **mineral structure** does not readily accommodate such ions.

(B) Regularities of distribution

Important features of general pattern of regularities, as revealed by many analyses of rock series are the following:

1) Cations with large radii and low charges tend to **substitute** for **potassium,** so are concentrated in **felsic** rather than mafic rocks, these elements (**Rb**, **Ba**) their abundance in a rock series is a good indication of the extent to which differentiation has sorted out constituent of the original magma.

2) Cations with smaller radii and with higher charges (e.g. **U**, **Th**, **Mo**, **W**, **Nb**, **Ta**, **Sn**, **Zr**) **cannot substitute any major elements**, so they concentrate at the **felsic end** of the series, because of their size and charge make it difficult for them to substitute for any major ions in common silicate minerals. These cations segregate in the late residual solutions, and if present in appreciable amounts they may form minerals of their own (e.g. uraninite, beryl, zircon, etc...).

3) Many elements with intermediate radius, **substitute** for **iron** and **magnesium**, and they are abundant in the earlier members of the differentiation sequence. For example some (**Cr**, **Ni**, **Co**) are strongly enriched with Mg in ultramafic rocks

4) Among the chalcophile elements, **few elements substitute** to some extent for **major elements** in silicate structures (e.g. Pb and Ti substitute for K - Bi substitute for Ca).

5) In a magma that contains **abundant sulfur**, part of the **chalcophile elements** may separate early in differentiation as an immiscible sulfide liquid

2- Trace Element Behaviour in Igneous Processes (During magmatic crystallization)

How can determine which kind of major element is substituted by kind of trace element?

Trace elements in magmas are those with a concentration usually below 0.1 wt.%. They are reported as elements, not as oxides, or using parts per million (ppm) or as part per billion (ppb) as concentration units.

The behavior of trace elements depends on whether they reside as traces in major minerals or are essential structural components in accessory minerals.

In igneous petrogenesis, the most frequently used trace elements include alkaline and alkaline earths (Li, Rb, Cs, Be, Sr, and Ba), transition elements of the first (Sc, V, Cr, Co, Ni, Cu, and Zn), second (Y, Zr, Nb, and Mo) and third series (Hf, Ta, and W) (B, Ga, and Ti) and rare earth elements (REE)

The distribution of trace elements in igneous rocks can provide important information about the origin and evolution of magmas. **Modern igneous petrologists commonly use trace-element studies for two purposes: -**

1. to model the behavior of minerals during a given igneous process, usually by means of trace-element fractionation equations
2. to identify the tectonic environment in which these magmas formed

The **behaviour** of the most important **trace elements** during the igneous processes **discuses briefly as following**: -

Rubidium: The only major element Rb can replace should be K. Rubidium forms no minerals of its own, being always incorporated in potassium minerals. Since Rb^+ is considerably larger than K^+, Rubidium is **admitted** into potassium minerals, and according the ratio increasing with the increasing differentiation; this ratio is highest in pegmatite feldspars.

Barium: Barium (Ba^{2+}) is too large (1.34 A) to replace Ca (0.99 A) or Na (0.97 A). But the only major element of comparable ionic size is potassium. On account of its higher charge Barium should be **captured by potassium** minerals and so Barium appears in biotite and potash feldspar. The available data indicate that barium being relatively enriched in early-formed potassium minerals.

Lead: lead is found in the silicate material of many igneous rocks, particularly in granites. It is evidently present at Pb^{2+} ion (1.20 A), diadochic with K^+. From the ionic charge alone it might be expected that the lead in magma would tend to be **captured** by potassium minerals.

Strontium: The size of the strontium ion (Sr^{2+} = 1.12 A) indicates that it can proxy for either calcium or potassium, being **admitted** (higher radius) to calcium minerals (plagioclase) or **captured** by potassium minerals (higher charge).

The data of geochemistry indicate that strontium in igneous rocks is present mostly in the plagioclase and that its concentrations increases as crystallization proceed. The admittance in place of calcium is the dominant process of removal of strontium from the magma. However, this process does not operate with all calcium minerals; for example pyroxene (suggesting that the pyroxene structure does not readily accommodate the strontium ion).

Zirconium: It characterizes by high charge and radius (0.79A), on this account zirconium does not enter into the common rock-forming minerals but appears in a specific phase, usually zircon. Zirconium is most abundant in later differentiates.

Cobalt: The cobalt ion is practically the same size (Co^{2+} = 0.72 A) as the **ferrous** ion (0.74 A), so cobalt should be **camouflaged** in ferrous minerals.

It is found that the Co: Fe ratio is greatest in early-formed ferrous minerals and decreases steadily with increasing fractionation. The major part of the cobalt in magma is removed in the early-formed minerals, especially olivine.

Nickel: The nickel ion (Ni^{2+} = 0.69 A) has essentially the same radius and the same charge as magnesium (Mg^{2+} = 0.66 A), and therefore should be **camouflaged** in magnesium minerals.

The ratio Ni : Mg is highest in early-formed magnesium crystals (especially olivine) and shows a steady decline in the later-formed minerals.

Lithium: Lithium follows magnesium, since the ionic sizes are nearly identical; because the lithium ion (Li^+ = 0.68 A) has a lower charge than the magnesium ion, it should be **admitted** into magnesium minerals

The Li : Mg ratio increase in later-formed minerals. Lithium is found in the mica and particularly the amphiboles. However, a considerable amount remains in the liquid until a very late stage of differentiation, since pegmatites often shows a particular concentration of lithium. Because of its single charge forms weaker bonds than the double charge on **Mg^{2+}** ; so the absence of **Li^+** in olivine and its common presence as a substitute for **Mg^{2+}** in the late stage of differentiation.

Vanadium: Vanadium is probably present in magmas as the V^{3+} ion (0.74 A). It is largely removed in magnetite, in which it replaces Fe^{3+} (0.64 A). Vanadium ionic radius is greater than ferric iron but its electronegativity is responsible for the enrichment of vanadium in early-formed magnetite.

Chromium: Chromium is also present in magma as the Cr^{3+} ion (0.63 A). Chromium ion is very close to that of Fe^{3+}, it is largely removed from magma in the early stage of crystallization as chromite, and chromium is also enriched in pyroxenes, especially those from ultrabasic rocks.

Titanium: In igneous rocks titanium is present mainly as ilmenite. Also it can replace **Al** and appears therefore in pyroxene, hornblende, and biotite. Titanium does not appear in muscovite, probably because in highly siliceous magmas, titanium is removed as **titanite** (Ca Ti Si O_4).

Hafnium: Hafnium (Hf^{4+} = 0.78 A) having the same charge and about the same radius as zirconium (Zr^{4+} = 0.79 A). It always occurs **camouflaged** in zirconium minerals. The Zr : Hf ratio remains almost constant throughout any process of fractional crystallization.

Germanium: The germanium ion has the same charge and somewhat higher radius than silicon (Ge^{4+} 0.53 A, Si^{4+} 0.42 A). Germanium replaces silicon, and the Ge : Si ratio in silicates minerals generally show little variations. Some degree of concentration of germanium in the late differentiates.

The Rare Earths: The charge and the comparatively large radius of The Rare Earths, coupled with their general low concentration, suggest that they would show relatively no tendency to replace the major elements during magmatic crystallization, and this is borne out by the concentration of Rare Earths as individual in pegmatites.

Table: summary of trace elements distribution (behavior**) during magmatic crystallization**

Rubidium	**Rb^+ = 1.47 A**	admitted into K^+= 1.33 A	
Barium	**Ba^{2+} = 1.34 A**	captured by K^+ = 1.33 A	not replace Ca^{2+}= 0.99A Na^+ = 0.97 A
Lead	**Pb^{2+} = 1.20 A**	captured by potassium minerals	
Strontium	**Sr^{2+} = 1.12 A**	admitted to calcium minerals (higher radius)	captured by potassium minerals (higher charge)
Zirconium	Zr^{4+} = 0.79 A	appears in a specific phase	does not enter into the common rock-forming minerals
Cobalt	**Co^{2+} = 0.72 A**	camouflaged in ferrous compounds (especially olivine)	Fe^{2+} = 0.74 A
Nickel	**Ni^{2+} = 0.69 A**	camouflaged in magnesium minerals (especially olivine)	Mg^{2+} = 0.66 A
Lithium	**Li^+ = 0.68 A**	admitted into magnesium minerals	Mg^{2+} = 0.66 A
Vanadium	**V^{3+} = 0.74 A** **Fe^{3+} = 0.64 A**	Due to the electronegativity	enrichment in early-formed magnetite

Chromium	**Cr^{3+} = 0.63 A** **Fe^{3+} = 0.64 A**	Due to the electronegativity	largely removed from a magma in the early stage
Titanium	**Ti^{4+} = 0.68 A** **Fe^{3+} = 0.64 A**	present mainly as ilmenite	It can replace **Al** and appears therefore in pyroxene, hornblende, and biotite
Hafnium	**Hf^{4+} = 0.78 A** **Zr^{4+} = 0.79 A**	camouflaged in zirconium minerals	ratio remains almost constant through process of crystallization
Germanium	**Ge^{4+} = 0.53 A** **Si^{4+} = 0.42 A**	Germanium replaces silicon	**Ge : Si** ratio in silicates minerals generally show little variations
The Rare Earths	**large radius and general low concentration**	show little tendency to replace the major elements during magmatic crystallization	

Chemical compositional variation in minerals (Minerals chemistry)

Minerals can form by one of the following processes:

- Precipitation from a fluid. This can take place within the Earth by hydrothermal processes and diagenesis, and at or near the Earth's surface as a result of evaporation, weathering, or biological activity.

- Sublimation from a vapor. This process is somewhat rare, but can take place at a volcanic vent, or deep in space where the pressure is near vacuum.
- During crystallization of magma either below or at the Earth's surface.
- Solid - Solid reactions. This process involves minerals reacting with other minerals in the solid state to produce one or more new minerals. Such processes take place due to changing in temperature and pressure conditions.

No matter what process is involved, a particular mineral cannot form unless the chemical components necessary to make the mineral are present. Thus, the most common minerals are minerals that have a chemical composition made of the common elements found in their environment.

Geochemistry was described as dealing with the abundance, distribution, and migration of the chemical elements in the earth. The basic units of geochemical investigation are thus the elements, either in the form of atoms or more often as charged particles or ions.

Atoms and ions have certain energy content which changes when they undergo physical or chemical transformations.

In redistribution and recombination of the chemical elements in minerals the atoms or ions lose part of their energy and yield more stable systems. After the development of reliable methods for the analysis of minerals, it was observed that many species are variable in composition.

In our definition of a mineral we said that a mineral has a definite, but not necessarily fixed chemical composition.

Generally chemical compositional variation in minerals is referred to ***solid solution***. Although most of us think of solutions as a liquid containing dissolved ions, solids can form solutions as well, in which case we think of one solid as being dissolved in another solid.

Solid solution

A solid solution is a homogeneous crystalline structure in which one or more types of atoms may be partly substituted for the original atoms without changing the structure of crystal.

A solid solution can be simply defined as a homogeneous crystalline solid of variable composition.

Solid solution occurs as the result of ions substituting for one another in a crystal structure.

In an ionic structure (structure of crystal), the structure is extended in three dimensional and any ion in the structure may be replaced by another ion of similar radius without causing any distortion of the structure

As with liquids, solids have different degrees of mutual solubility, depending on their chemical properties and crystalline structure, which determine how their atoms fit together in the crystal lattice.

The substances may be soluble over a partial or complete range of relative concentrations, producing a crystal whose properties vary continuously over the range.

The factors that control the amount of solid solutions:

The factors that control the amount of solid solution that can take place in any crystal structure is determined by:-

1) The ionic radius
2) The charges on the ions
3) The temperature of formation and pressure
4) The nature of the structure of crystal

1-The nature of the structure of crystal

The nature of the structure of crystal has considerable influence on the degree of atomic substitution, some structures, such as **spinel** and **apatite** are well known for extensive atomic substitution, whereas other structure such as **quartz** shows very little atomic substitution. In part this phenomenon is due to the lack of foreign ions of suitable size and charge.

2-The ionic radius

The size of the ions and the size of the crystallographic sites into which they substitute are more important on the degree of substitution.

Ionic size has a fundamental influence on the degree of substitution, since the substituting ion must be able to occupy the lattice position without causing distortion of the structure.

From a study of many mixed crystals it has been found that, the radius of substituting and substituted ions do not differ by more than 15%. For example, Mg^{2+} and Fe^{2+} have a size difference less than 10 %, and complete solid solution between these two elements is observed in a wide range of minerals. However, the size difference between Ca^{2+} and Mg^{2+} is more than 30 %, and we expect no or very little substitution of Mg for Ca to occur in minerals. Generally ions of about the same size can substitute for one another.

The size of the crystallographic site can also play a role if one of the ions is of nearly the same size, but is too large to fit into the site, so this influence on the degree of substitution.

3-The charges on the ions

The amount of solid solution is influenced by the charges on the ions that are substituting for one another.

If the charges of ions are the same, then the crystal structure can remain electrically neutral. If the charges are not the same, then other substitutions must take place to maintain charge balance.

Generally, little or no atomic substitution takes place when the difference in charge on the ions is ***greater than one***, even when size is appropriate (e.g. Y^{3+} does not substitute for Na^{+}); this because of the difficulty in balancing the charge requirements by other substitutions.

4-The temperature and pressure

The temperature of formation of the substance at which the substitution takes place has considerable influence on the degree of atomic substitution.

Generally, there is a greater amount of substitution **takes place at higher temperature**. For a specific mineral the degree of atomic substitution has been determined for different temperatures, the composition of mineral may indicate the temperature of formation.

High temperatures favour the formation of solid solutions, so that end members which are immiscible at low temperature may form complete or more extensive solid solutions with each other at high temperature. High temperatures promote greater atomic vibration and open structures, which are easier to distort locally to accommodate differently-sized cations.

The amount of ***titanium*** in solid solution in ***magnetite*** as a function of **temperature** is known from laboratory investigation.

Magnetite is a common ore mineral provided the ore-forming solutions contained sufficient titanium to saturate the magnetite, **and the titanium content of the mineral will indicate the temperature conditions during formation of Magnetite.**

Pressure can also have an effect because it can change the size the crystallographic sites, thus resulting in different substitutions than might take place at lower pressure.

Types of solid solution

1-Substitutional solid solution

2-Interstitial solid solution

3-Omission solid solution

1-Substitutional solid solution

1. A- Simple substitution

When ions of equal charge and nearly equal size substitute for one another, the solid solution is said to be simple substitution.

Generally if the sizes of the ions are nearly the same, the solid solution can occur over the complete range of possible compositions and the solid solution series is said to be **complete solid solution**. For example, common olivine may be described as a solid solution of Mg_2SiO_4(**Forsterite**) and Fe_2SiO_4(**Fayalite**), and the accurate composition of any sample of olivine may be stated in terms of these end-members, such as $Fo_{85}Fa_{15}$, this is, $(Mg_{0-.85}Fe_{0.-15})_2SiO_4$.

<u>The substitution may only occur over a limited range of compositions</u> and the solid solution series is said to be **partial** or **limited solid solution**.

<u>Partial or limited solid solution can also occur because the substituting ion does not occur in high enough concentrations in the environment in which the mineral is formed</u>.

<u>The replace ability of ions may be complete or partial</u>; and the degree of ionic substitution depends on:-

1) the temperature

2) the availability of substituting ions

3) radius and charge of ions

The useful term **diadochic** has been introduced to describe the ability of different elements to occupy the same lattice position in a crystal. For example, in olivine structures an **iron ion** may completely replace the **magnesium ion**. Also **Mg**, **Fe**, and **Mn** are diadochic in the structure of dolomite.

The concept of diadochy, always applies to a particular structure; two elements may be diadochic in one mineral and not in another.

1. B- Coupled Substitution

Coupled substitution occurs if ions of different charge are substituted. It is a substitution of two or more elements in a crystalline compound, which maintains electrical neutrality (having to make another substitution in order to maintain charge balance). Such coupled substitution is common in the silicate minerals where Al^{+3} substitutes for Si^{+4}.

For example, in the amphibole mineral tremolite - $Ca_2 Mg_5 Si_8 O_{22}(OH)_2$, if Al^{+3} replaces one of the Si^{+4} ions then Na^{+1} can go into a site that is normally vacant to maintain charge balance. The resulting formula would be $Na\,Ca_2\,Mg_5\,Al\,Si_7\,O_{22}\,(OH)_2$. This would be called a sodic amphibole.

In passing from albite ($NaAlSo_3O_8$) to anorthite ($CaAl_2Si_2O_8$); Ca^{2+} substitutes for Na^+ and electrical neutrality is maintained by the coupled Substitution of Al^{3+} for Si^{4+}; similarly, in diposide ($CaMgSi_2O_6$), Mg^{2+}-Si^{4+} may be replaced in part by Al^{3+}-Al^{3+}.

Such coupled subsituations are especially common in silicate minerals and made the interpretation of their composition exceedingly difficult before this phenomenon was recognized and understood.

2- Interstitial substitution or interstitial solid solution

In **interstitial solid solution**, atoms or ions do not replace ions in the structure but fit into interstices in the lattice.

Interstitial solid solution takes place when ions fill the interstices (voids) found between the ions, or ionic groups of a crystal structure. The interstices may take the form of channel-like cavities in certain crystals, such as the ring silicate **beryl** mineral…..etc.

Interstitial solid solutions are solid state solutions that form when solute atoms enter into the holes between solvent atoms of crystal lattice.

Since minerals usually crystallize from solutions containing many ions other than those essential to the mineral, they often incorporate some foreign ions in the structure.

For example: **Beryl**: $Be_3Al_2Si_6O_{18}$: where amount of K , Rb and Cs are reported in **Beryl** analysis, housed interstitially in the hexagonal channels (can substitute into center of ring).

$Si \longleftrightarrow Al + R$ **where** $R := K^+$, Rb^+ or Cs^+

The main difference between substitutional and interstitial solid solution, substitutional solid solutions are solid-state solutions that form when the solute atoms replace the solvent atoms. This type of solid solutions forms only if the solute atoms are enough to replace the solvent atoms in the crystal lattice. Moreover, the atomic size of solutes is nearly similar to the size of solvent atoms. But In an interstitial solid solution, by contrast, **the atoms** of the solvent are bigger than the solute and the solute atoms fit into the gaps or interstitial spaces between the solvent atoms.

3-Omission solid solution

Omission solid solution occurs when an ion of higher charge substitutes for an ion of lower charge. Omission solid solution occurs when a more highly charged cation replaces two or more other cations for charge balance. In order to maintain charge balance, two of the lower charged ions will be replaced, but the higher charged ion will occupy only one site, thus the other site will become vacant, or omitted.

An example of this type of solid solution is found in the blue variety of microcline (Amazonite), in which a **Pb^{+2}** ion replaces **$2\ K^{+1}$** ions. One of the K^{+} sites is replaced by the Pb^{+2} and the other site is left vacant.

$$\mathbf{K + K \longleftrightarrow Pb^{2+}}$$

What are the properties which change with solid solution?

- **Color**: especially in minerals in which Mg and Fe^{+2} substitutes for one another. For example, in the series tremolite-actinolite, tremolite is white in color (Mg end member) and actinolite is dark green.
- **Specific Gravity**: As a heavier ion substitutes for a lighter one, the specific gravity of the mineral will change. For example, in the mineral olivine, specific gravity varies from 3.3 (**Forsterite**) to 4.4 (**Fayalite**).
- **Hardness**: The hardness may change because of the different bond strengths.
- **Temperature of melting**: The strength of the cation-oxygen bond determines the melting point of the mineral, e.g. **Forsterite** melts at a much higher temperature than **Fayalite**.

Exsolution

As mentioned above, the extent of solid solution is dependent on temperature and pressure since the sizes of ions and the sizes of the crystallographic sites can change with temperature and pressure. Thus, some minerals show complete solid solution under one set of temperature /

pressure conditions, and only limited solid solution under different temperature /pressure conditions.

When the conditions change to those where limited solid solution is favored, the mineral exsolves or is unmixed. But, because the process is taking place in the solid state, exsolution or unmixing cannot easily form two separate phases, because the ions must diffuse through the solid.

In fact, what happens is that two separate phases form in discrete domains within a single mineral crystal. These domains are crystallographically oriented, so they appear as lamellae or lines across the mineral grain.

Exsolution in generally, is the process through which a homogeneous solid solution separates into at least two different crystalline minerals without the addition or removal of any elements. In most cases, Exsolution occurs upon cooling.

The alkali feldspars (albite -$NaAlSi_3O_8$ -orthoclase-$KAlSi_3O_8$) form a complete solid solution at high temperature, but at lower temperature the solid solution becomes progressively more limited, and as a result lamellae of albite-rich feldspar begin to grow in the orthoclase-rich alkali feldspar. This produces a texture called ***perthite***, where the lighter colored albite-rich feldspar is seen to occur as irregular lines or streaks (the lamellae) within the pink orthoclase-rich feldspar. In the case of perthite, the exsolution lamellae are often large enough to see with the naked eye, in other systems, the exsolution lamellae can only be observed with the petrographic microscope

Chemistry of principal minerals and mineral groups

A mineral is a naturally-occurring substance formed through geological processes that has a defined chemical composition and a highly ordered atomic structure. **To be classified as a true mineral, must follow these general rules :**

1. A substance must be a solid
2. It must also a naturally occurring and homogeneous substance
3. Has a definite chemical composition
4. Its atoms are arranged into a definite pattern (a crystalline structure) called a crystal

Minerals are naturally occurring chemical compounds in which atoms are arranged in three-dimensional patterns. The kind of elements and their arrangements lead to a particular appearance and certain properties for each mineral.

The same chemical elements when arranged in different crystal patterns show different characteristics. Classic examples are minerals made of the element carbon (C), flat planes of carbon atoms form the mineral graphite, which is a gray and soft material. Carbon atoms arranged in a different pattern to form the mineral diamond -- the hardest natural substance known.

Scientists can distinguish more than 4,000 different minerals but many are very rare. About 200 minerals make up the bulk of most rocks. The most abundant minerals which are more common in igneous rock (Silicates minerals which contain silicon, oxygen and usually one or more other elements), are **silica minerals**, **olivine**, **feldspars**, **pyroxenes**, **amphiboles and micas**.

The mineralogical composition is a basic criterion in the classification of igneous rocks. **Chemistry of principal minerals and mineral groups are now discussed in the following:**

Chemical variations in the olivine minerals

The olivine group crystallizes in **orthorhombic** system. They have a number of species:

Forsterite	Mg_2SiO_4	**Tephroite**	Mn_2SiO_4
Fayalite	Fe_2SiO_4	**Monticellite**	$CaMgSiO_4$
Olivine	$(Mg, Fe)_2 SiO_4$	**Glaucochroite**	$CaMnSiO_4$

The only common rock-forming minerals are the magnesium-iron compounds. The other species are known from ore deposits in metamorphic limestones.

X-ray studies on olivine show that is built of independent SiO_4 tetrahedra and the magnesium and ferrous ions lie between groups.

The olivine group has no tendency to form fibrous or platy crystals and generally occur as equidimensional crystals.

Olivines belong the Nesosilicates and their structures consist of independent ($Si0_4$) tetrahedra linked together by divalent Fe and Mg atoms.

Olivines form a complete solid solution series between ***Forsterite*** (Mg_2Si0_4) and ***Fayalite*** (Fe_2SiO_4) and general formula (Mg, Fe)$_2$ $Si0_4$. The members of this series are known as Olivines, and there are four intermediate members of olivines that are recognized between ***Forsterite*** and ***Fayalite*** based on the ratio **Mg** to **Fe**$^{2+}$.

As a general rule of replacement, if the size difference between the ionic radii of ionic radii elements is less than 15%, then extensive solid solution is possible. For example, **Mg** and **Fe**$^{2+}$ have similar ionic radii, and size difference of around 8% and complete solid solution between these two elements is observed in a wide range in olivine group.

If there is a large size difference between the ionic radii of elements (more than **>** 15%), then the crystal structure has to deform locally (strain) to accommodate a large cation in a small site and vice versa. This strain increases the difficulties for achievement the solid solution. For example, Ca^{2+} has an ionic radius more larger than Mg, and very little substitution of Mg for Ca to occur in olivine group. Very small quantities of replacement of (**Mg** and **Fe^{2+}**) by **Mn** may occur in minerals of the olivine group.

Silicon in olivine structure is **not** replaced by **aluminium** as in chain and sheet silicates.

Generally The cation positions in olivine crystals are almost exclusively occupied by divalent atoms , but trivalent **Al** and Fe^{3+} atoms are absent in olivine structures.

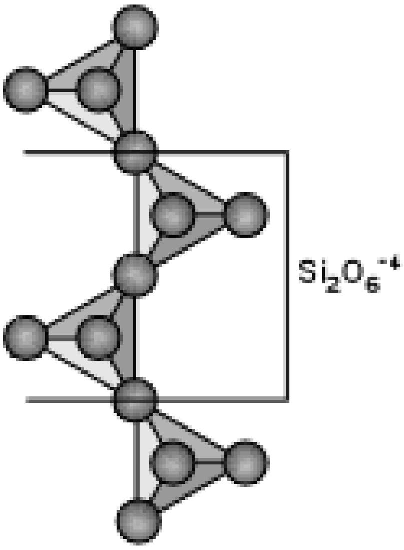
Olivine crystals commonly show zonation: **Mg**-rich core is usually surrounded by a **Fe**-rich rim, but inversion of the zonation is not normally.

Generally, the composition of olivine group corresponds closely to $(Mg, Fe)_2 SiO_4$, sometimes shows little replacement by other elements.

Chemical variations in the pyroxene minerals

The pyroxenes are group of minerals closely related in physical properties, as well as in chemical composition, although they crystallize in two different systems, **orthorhombic** and **monoclinic**.

The tetrahedral SiO_4 groups are linked together into chains by the sharing of one oxygen atom between two adjacent groups. The silicon- oxygen chains lie parallel to the vertical crystallographic C-axis and are bounded together laterally by the metal ions. The prismatic habit of pyroxene crystals is a consequence of this internal structure.



The chemical composition of pyroxenes can be expressed by the general formula **(W) (X, Y) Z_2O_6**, in which the symbols W, X, Y and Z indicate elements having similar ionic radii and capable of replacing each other in the structure. In the pyroxenes these elements may be:

W: Na, Ca

X: Mg, Fe^{2+}, Li, Mn

Y: Al, Fe^{3+}, Ti

Z: Si, Al (in minor amount)

On the basis of chemical composition, **the following species** are recognized:

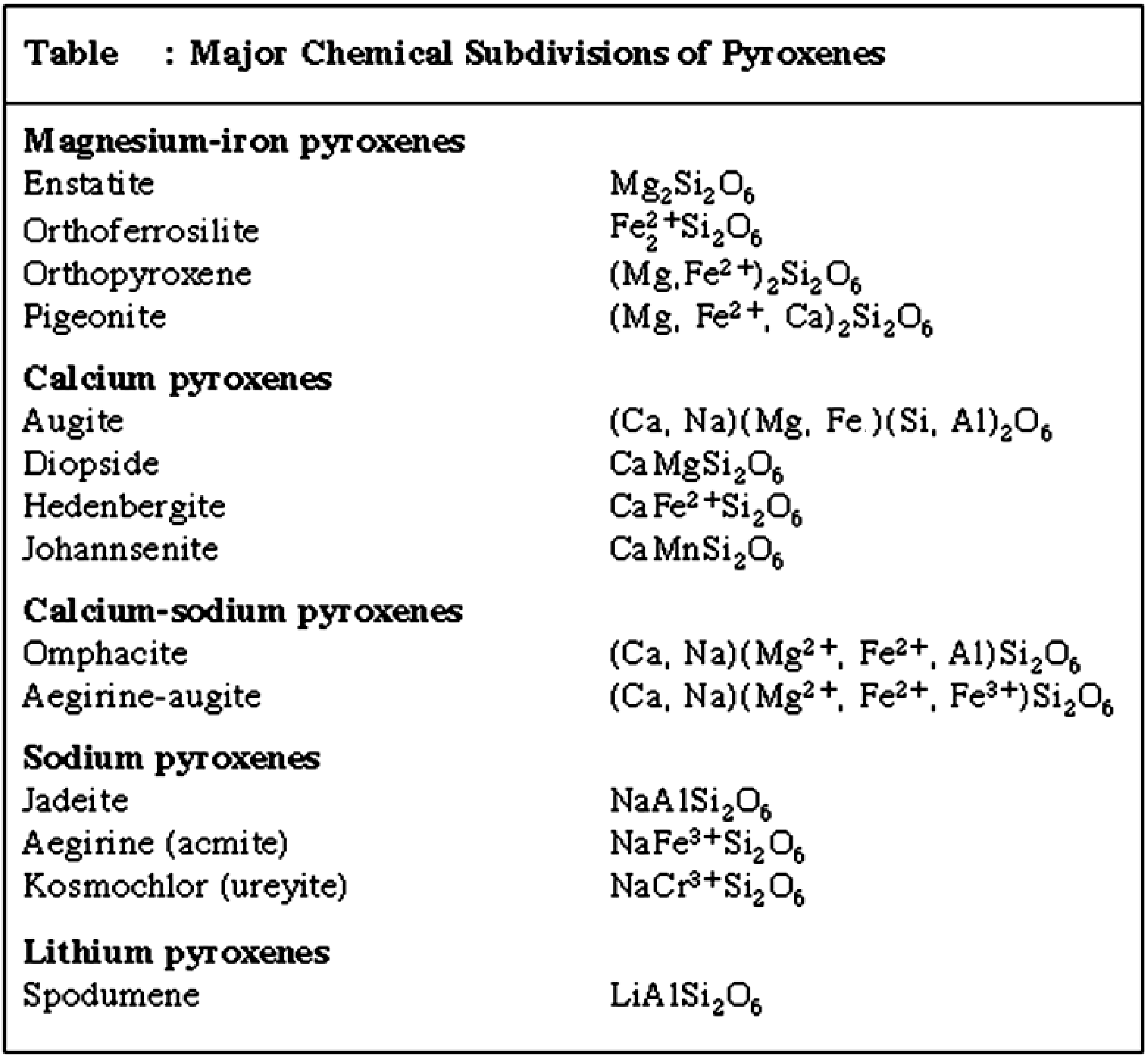


Table : Major Chemical Subdivisions of Pyroxenes

Magnesium-iron pyroxenes	
Enstatite	$Mg_2Si_2O_6$
Orthoferrosilite	$Fe^{2+}_2Si_2O_6$
Orthopyroxene	$(Mg,Fe^{2+})_2Si_2O_6$
Pigeonite	$(Mg, Fe^{2+}, Ca)_2Si_2O_6$
Calcium pyroxenes	
Augite	$(Ca, Na)(Mg, Fe)(Si, Al)_2O_6$
Diopside	$CaMgSi_2O_6$
Hedenbergite	$CaFe^{2+}Si_2O_6$
Johannsenite	$CaMnSi_2O_6$
Calcium-sodium pyroxenes	
Omphacite	$(Ca, Na)(Mg^{2+}, Fe^{2+}, Al)Si_2O_6$
Aegirine-augite	$(Ca, Na)(Mg^{2+}, Fe^{2+}, Fe^{3+})Si_2O_6$
Sodium pyroxenes	
Jadeite	$NaAlSi_2O_6$
Aegirine (acmite)	$NaFe^{3+}Si_2O_6$
Kosmochlor (ureyite)	$NaCr^{3+}Si_2O_6$
Lithium pyroxenes	
Spodumene	$LiAlSi_2O_6$

On the **basis of chemical composition and crystal system**, the following species are recognized:

Orthorhombic pyroxenes

Enstatite	$Mg_2Si_2O_6$
Hypersthene	$(Mg, Fe)_2 Si_2O_6$

Monoclinic pyroxenes

Clinoenstatite	$Mg_2Si_2O_6$
Clinohypersthene	$(Mg, Fe)_2\ Si_2O_6$
Diopside	$CaMgSi_2O_6$
Hedenbergite	$CaFe^{2+}Si_2O_6$
Augite	$(Ca,Na)(Mg,Fe\ ,Al,Ti)(Si,Al)_2O_6$
Pigonite	$(Mg, Fe^{+2}, Ca)_2\ Si_2O_6$
Aegirine	$Na\ Fe^{3+}\ Si_2O_6$
Jadeite	$Na\ Al\ Si_2O_6$
Spodumene	$Li\ Al\ Si_2O_6$
Johannsenite	$CaMn\ Si_2O_6$

Orthopyroxene has always been considered to be Ca-poor pyroxene. The orthorhombic pyroxenes range in composition from pure $Mg_2Si_2O_6$ *(enstatite)* to about 90% $Fe_2Si_2O_6$ (*ferrosilite*), because the pure compound $Fe_2Si_2O_6$ is not a stable phase at high temperatures.

The common orthopyroxenes of igneous rocks are all magnesium-rich.

The orthorhombic pyroxenes have been divided into number of subspecies based on composition, similar to the division of the plagioclase series.

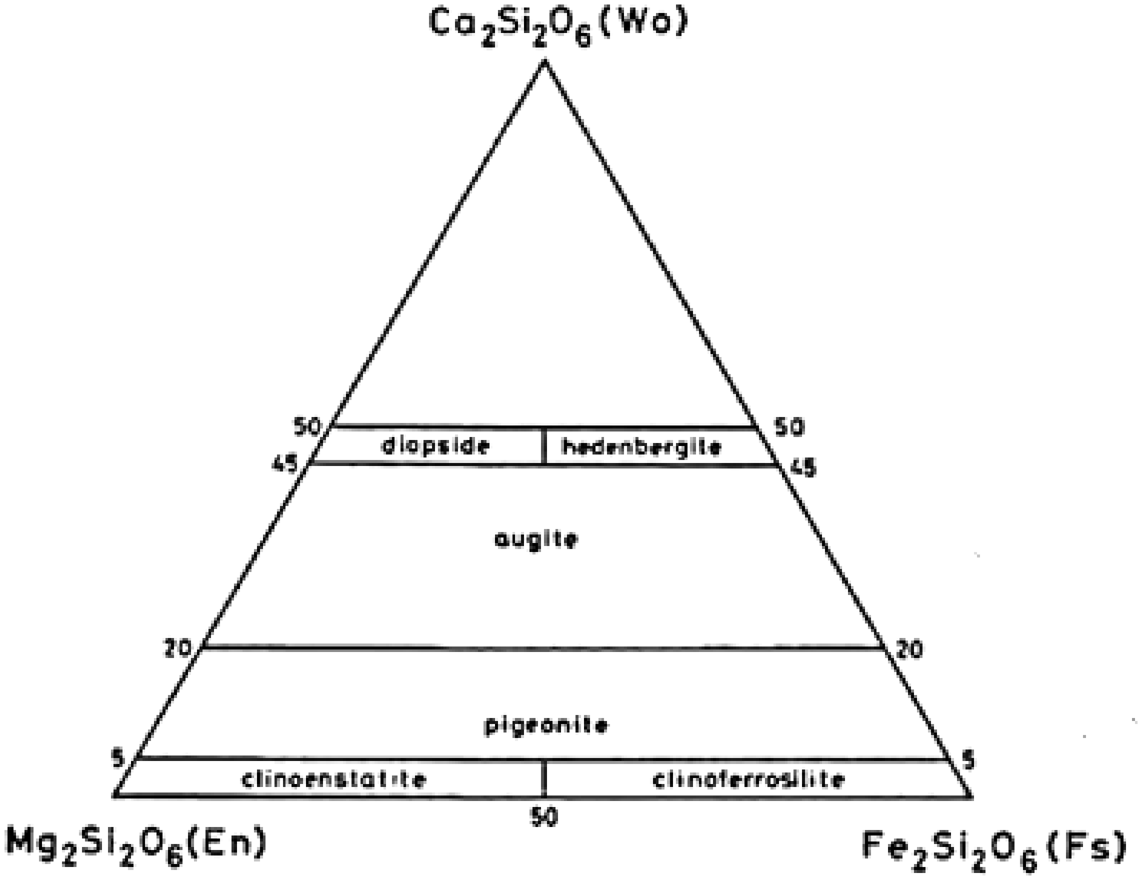
The diopside and hedenbergite series is well established throughout the whole range in composition, and a limited amount of aluminum can enter into this series, and such aluminous pyroxenes are called augite.

The aegirine is connected with the augite by members of intermediate composition, which are grouped **under the name aegirine-augite**.

In volcanic rocks the pyroxenes may be low-calcium augite, whereas in plutonic rocks the pyroxenes are normal augite and/or orthorhombic pyroxenes.

The most common pyroxenes can be represented as part of the chemical system $CaSiO_3$ (**wollastonite**), $MgSiO_3$ (**enstatite**), and $FeSiO_3$ (**ferrosilite**).

Since no true pyroxenes exist with calcium contents greater than that of the diopside and hedenbergite.



Composition ranges of the Ca-Mg-Fe clinopyroxenes with accepted names.

The main substitution in pyroxenes:

A)-Ferrous iron and magnesium substitute in pyroxenes

B)-Aluminum substitution in pyroxenes

A - Ferrous iron and magnesium substitute in pyroxenes

Ferrous iron and magnesium substitute freely in pyroxenes because they have similar ionic sizes and charges. Complete substitution exists between **enstatite** ($Mg_2Si_2O_6$) and **ferrosilite** ($Fe_2Si_2O_6$), and complete solid solution of iron for magnesium exists between **diopside** ($CaMgSi_2O_6$) and **hedenbergite** ($CaFeSi_2O_6$).

Augite is related to members of the diopside-hedenbergite series with limited substitution of Na^+ for Ca^{2+}, Fe^{2+} for Mg^{2+} and Al^{3+} for Si^{4+}.

The coupled substitution of Na^+ and Al^{3+} for 2 Mg^{2+} in **enstatite** produces the pyroxene **jadeite**.

The coupled substitution of Na^+ and Fe^{3+} for 2 Mg^{2+} in **enstatite** produces the pyroxene **aegirine** (acmite).

Substitution of Li^+ and Al^{3+} for 2 Mg^{2+} yields **spodumene**.

B- Aluminum substitution in pyroxenes

The nature of aluminum substitution in pyroxenes varies significantly from one pyroxene to another.

In the ortho - pyroxene, usually no aluminum is present, or present in only small amounts.

In augite there can be extensive substitution of aluminum for silicon.

In both jadeite and spodumene, which contain aluminum in the **Y** site, but the substitution of silicon by aluminum in the **Z** tetrahedral site is negligible.

Exsolution in pyroxenes

At high temperatures, pyroxenes have more extensive fields of solid solution than they do at lower ones. Therefore, as temperatures decrease, the pyroxene adjusts its composition in the solid state by **exsolving** a separate phase in the form of lamellae within the host pyroxene crystal.

The lamellae are exsolved along specific crystallographic directions, producing oriented intergrowths texture.

There are five principal of exsolution:

(1) **Augite** with **enstatite** lamellae

(2) **Augite** with **pigeonite** lamellae

(3) **Augite** with both **pigeonite** and **enstatite** lamellae,

(4) **Pigeonite** with **augite** lamellae

(5) **Enstatite** with **augite** lamellae

The relation between geochemical systems and occurrence of common pyroxenes as the following :

Magnesium-rich orthopyroxenes occur in the earlier-formed rocks of ultramafic complexes. They are important constituents of basalts, gabbros, norites and peridotites.

Augite is the most common pyroxene and is found primarily in mafic igneous rocks. It occurs in basalts, gabbros, andesites, diorites, and peridotites. The augites in layered ultramafic intrusions show compositional trends of increasing iron and decreasing magnesium contents with fractionation.

Aegirine and **aegirine-augite** occur most commonly as products of the crystallization of alkaline magmas. They are found in alkalic rocks such as nepheline syenites, and they are associated with feldspathoids, and sodium-rich amphiboles.

Pigeonites are common in high-temperature, rapidly cooled volcanic lavas, and in some intrusive rocks such as diabases. Pigeonites can occur as exsolution lamellae in augites of more slowly cooled igneous rocks.

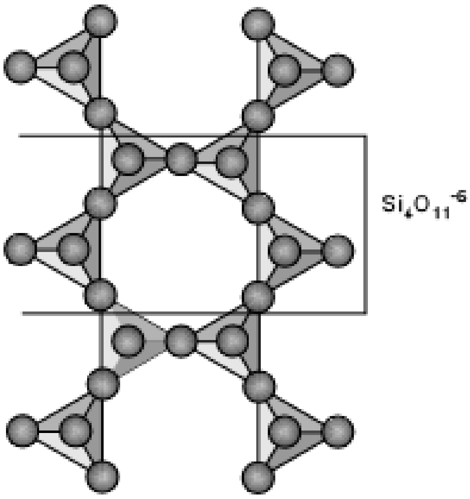
Spodumene is found almost exclusively in lithium-rich pegmatites and ore bodies. Spodumene is generally associated with albite, muscovite and tourmaline.

Chemical variations in the amphibole minerals

The amphiboles group comprises a number of species, which, although falling both in **orthorhombic** and **monoclinic** systems, are closely related in crystallographic and other physical properties, as well as in chemical composition. They form isomorphous series, and extensive replacement of one ion by others of similar size can take place, giving rise to very complex chemical compositions.

The amphiboles contain (OH) group in their structure, and the Si : O ratio is 4 : 11, not 1 : 3 as in the pyroxenes.

The fundamental unit in their structure is a double chains with alternate tetrahedra linked by the sharing of the oxygen, giving rise an Si : O ratio is 4 : 11. In the structure these double chains lie parallel to the vertical crystallographic axis and are bounded together laterally by the metal ions.



A general formula for all members of the amphiboles group can be writing as; **$(W\ X\ Y)_{7-8}\ (Z_4O_{11})_2\ \ (OH, F)_2$**, in which the symbols W, X, Y indicate elements having similar ionic radii and capable of replacing each other in the structure.

W stands for the large metallic cations Ca and Na (K is sometimes present in small amounts)

X stands for the smaller metallic cations Mg and Fe^{2+} (sometimes Mn).

Y stands for Ti, Al and Fe^{3+}.

Z stands for Si and Al.

In the generally, the degree of atomic substitution is as the following:

1 - **Al** may replace **Si** in the **Si_4O_{11}** chains to extent of Al **Si_3O_{11}** (the amount of **Al** replacement is function of conditions of formations

2-The high-temperature amphiboles can be more aluminous than low-temperature amphiboles.

3- **Fe^{2+}** and **Mg** are completely interchangeable.

4- Total (**Ca, Na**) vary between amphibole minerals.

5- **OH** and **F** are completely interchangeable.

On the basis of chemical composition and crystal structure, the following species are recognized in amphiboles:

Orthorhombic

Anthophyllite series $(Mg, Fe)_7 (Si_4O_{11})_2 (OH)_2$ (Mg predominant over Fe).

Monoclinic

Cummingtonite series $(Fe, Mg)_7 (Si_4O_{11})_2 (OH)_2$ (Fe predominant over Mg).

Tremolite $Ca_2 Mg_5 (Si_4O_{11})_2 (OH)_2$

Actinolite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$

Hornblende series $Ca_2 Na_{0-1} (Mg Fe, Al)_5 [(Al, Si)_4O_{11}]_2 (OH)_2$

Glaucophane $\mathbf{Na_2}\, Mg_3Al_2 (Si_4O_{11})_2 (OH)_2$

Ribeckite $\mathbf{Na_2}\, Fe_3^{2+} Fe_2^{3+} (Si_4O_{11})_2 (OH)_2$

Arfvedsonite $\mathbf{Na_3}\, (Fe^{2+}, Mg)_4 Fe^{3+} (Si_4O_{11})_2 (OH)_2$

Alkali amphiboles series

The anthophyllite series corresponds to orthorhombic - hypersthene series in pyroxene group. The ratio **Mg : Fe** ranges from 7 : 0 up to about 1 : 1. Al is often present and can replace Si in (Si_4O_{11}) to form ($Al\ Si_3O_{11}$). Members of the anthophyllite series have been found only in metamorphic rocks.

In the cummingtonite series, the ratio **Fe : Mg** ranges from 7 : 0 up to about 1:2. Members of the cummingtonite series are also confined in metamorphic rocks.

Tremolite and **Actinolite** are two very similar minerals that form a series with each other and essentially share the same chemical formula. **Tremolite** has a greater presence of Magnesium over Iron, whereas **Actinolite** has a greater presence of Iron over Magnesium**.**

The **Tremolite series** corresponds to the diopside-hedenbergite series in the pyroxene group. In tremolite magnesium is replaceable by ferrous iron and also in part by aluminum and ferric iron, silicon in part by aluminum, and additional sodium ion may enter the structure.

The mineral known as hornblende (**hornblende series)** has a very wide range of composition, most hornblende is green, but there is dark brown variety (known as basaltic hornblende), which is sometimes considered as a separate series.

The **alkali amphiboles** can be considered as derived from the hornblende series by the partial or complete substitution of Na for Ca.

Amphiboles occur more often in plutonic rocks than in volcanic rocks, because the incorporation of OH group in the structure is favored by the crystallization under pressure.

The major chemical subgroups of amphiboles

The mineral nomenclature and classification of the amphiboles is divided into **four principal subdivisions** based on the chemistry of the **X and W** cations in general formula of amphiboles leading to more than 70 defined minerals:

(1) Iron -manganese amphibole group

X site is occupied by Fe, Mg, Mn we have Iron-magnesium amphiboles e.g.:

Anthophyllite $(Mg, Fe)_7 Si_8O_{22}(OH)_2$

Cummingtonite $(Fe , Mg)_7 Si_8O_{22}(OH)_2$

(2) Calcic amphibole group

If **W** site is occupied by Ca we have calcium amphiboles e.g.:

Tremolite $Ca_2 Mg_5 (Si_4O_{11})_2 (OH)_2$

Hornblende $Ca_2 (Mg Fe, Al)_5 [(Al, Si)_4O_{11}]_2 (OH)_2$

(3) Sodic-calcic amphibole group

If **W** sites is occupied by Ca and Na - Calcium-Sodium amphiboles e.g.:

- **Richterite** $Na(Na,Ca)Mg_5Si_8O_{22}(OH)_2$

(4) Sodic amphibole group.

If **W** sites is occupied by Na we have Sodium or alkali amphiboles

e.g.: **Riebeckite** $Na_2 Fe_3^{2+} Fe_2^{3+} Si_8O_{22}(OH)_2$

Because of the wide range of chemical substitutions in the crystal structure, amphiboles can crystallize in igneous and metamorphic rocks with a wide range of bulk chemistries.

The chemical difference between pyroxenes and amphiboles

The pyroxenes differ compositionally from the amphiboles in:

1- The basic **structure** in the amphibole is a double chain of tetrahedra (the single chain structure of pyroxene)

2- Pyroxenes **contain no** essential water in the form of hydroxyls in their structure, whereas amphiboles are considered to be hydrous silicates.

3-Chemical difference between the two groups is based on the presence of cations in **W site. In** amphiboles **W site** contain the alkali elements, typically **sodium** and at sometimes **potassium**; but the **pyroxenes cannot** accommodate **potassium in W site**.

4- **Hydroxyl** groups in the amphibole structure decrease their thermal stability relative to the pyroxenes.

5- At **high temperatures** amphiboles decompose to anhydrous minerals, but at high temperatures, pyroxenes have more extensive solid solutions.

Chemical variations in the silica minerals

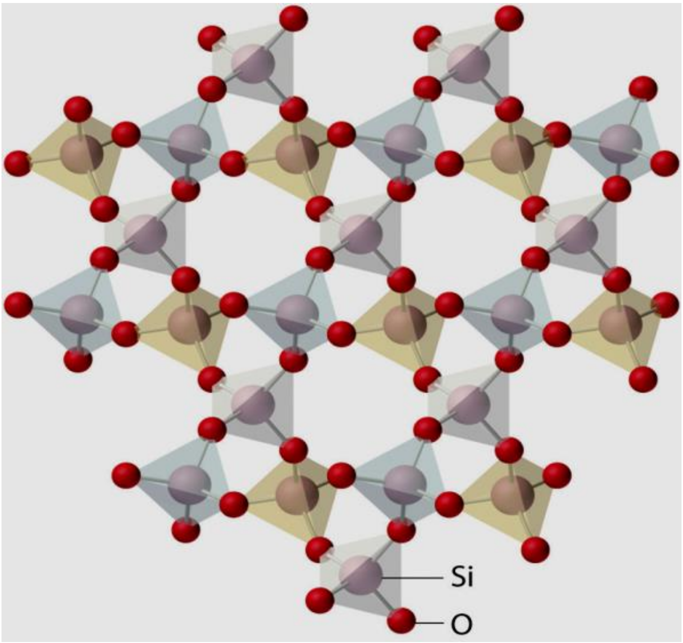
Silica occurs in nature as **seven** distinct minerals. **Quartz** is very common; **tridymite** and **cristobalite** are widely distributed in volcanic rocks.

Cosite and **stishovite** are high-pressure forms first mad in the laboratory.

Opal is obtained by deposition from aqueous silica solutions at low temperatures. It is deposited by thermal waters associated with igneous activity, and **Opal** is a mineral consisting of hydrated amorphous silica with the chemical formula **$SiO_2.nH_2O$. Silica glass** is very rare.

Quartz, cristobalite and tridymite are the forms of silica that may occur in igneous rocks, these three polymorphs of silica are all built of tetrahedral groups of four oxygen atoms surrounding a central silicon atom.

The silicon-oxygen tetrahedral are linked together to form a three-dimensional network, but the pattern of linkage is different for each form, so the difference in their crystal structures and their properties (α-quartz: **Trigonal** - β-quartz: **Hexagonal** - cristobalite: **Tetragonal** - tridymite: **Triclinic**)



The basic structural element of silica is the SiO_4 tetrahedron. Quartz consists of interconnected SiO_4 tetrahedra that build up a rigid three-dimensional network.

There are many possible ways of connecting SiO_4 tetrahedra different from that found in quartz, realized in various other silica polymorphs. Since all of them consist of a three-dimensional SiO_4 network, all are classified as **network silicates**

Of all silica polymorphs, quartz is the only stable form at normal conditions, and all other silica polymorphs will - given sufficient time to transform into quartz. The other polymorphs are stable at different and sometimes very special conditions, mostly under high temperatures and high pressures.

Theoretically, trigonal quartz (**α-quartz**) will transform into hexagonal **β- quartz** at 573°C, upon further heating the SiO_2 will transform into **tridymite (**Triclinic system**)** at 870°C and later to **cristobalite (**Tetragonal system**)** at 1470°C. At 1705°C cristobalite finally melts.

The transitions of one silica polymorph into another require the chemical bonds to be broken up and reconnected to alter the crystal structure. Accordingly, such a transition is called **reconstructive**.

In general, complete reconstructive transitions between polymorphs need a lot of time. Quick changes in temperature do not allow for the complete rebuilding of the crystal structure, and the transition will be skipped. This is what happens when **β**-quartz directly melts at 1750°C without transformation into tridymite

Quartz is the stable phase of silica under the physical conditions that prevail over most of the Earth’s crust.

Coesite occurs at great depth, generally in the upper Earth’s mantle. Stishovite would require even greater depths of burial, and no rocks that occur on the terrestrial surface have been buried, so Stishovite is reported only in a few localities that were subjected to very high pressures from meteorite impact events.

Quartz shows less range in chemical composition than do most other minerals, it commonly contains parts per million of aluminum atoms substituting for silicon atoms, with charge balance maintained by the incorporation of small atoms, such as sodium.

Chemical variations in the feldspar minerals

The feldspars are the most common of all minerals. They fall into two groups; **the potassium feldspars**, which are monoclinic in symmetry, and **the sodium and calcium feldspars** (the **plagioclases**), which are definitely triclinic. A point of great interest is the solid solution between albite ($NaAlSi_3O_8$) and anorthothite ($CaAl_2Si_2O_8$), and the feldspars of intermediate composition were mixed crystals of these two components, where that Na Si often substitutes for Ca Al.

The general formula for the feldspars can be written as **WZ_4O_8**, in which

W may be Na, K, Ca and Ba.

Z is Si and Al.

All the **W** ions are big and much larger than iron or magnesium, which are too small to occupy the voids in the structure fully.

The Si: Al ratio vary from 3 : 1 to 1 : 1. The structure of feldspars is a continuous three-dimensional network of **SiO_4** and **AlO_4** tetrahedra, with the positively charged sodium, potassium, calcium and barium situated in the interstices of the negatively charged network.

The feldspars may be discussed as a three-component system, the component being $KAlSi_3O_8$ (**orthoclase**), $NaAlSi_3O_8$ (**albite**) and $CaAl_2Si_2O_8$ (**anorthothite**). Complexities are introduced by the solid solution relations existing among these three components.

The potash- feldspar minerals occur in several forms having different optical and physical properties. ***Sanidine***, the monoclinic high-temperature polymorph, occurs in volcanic rocks. ***Orthoclase***, another monoclinic variety and ***microcline*** (triclinic) are found in wide variety of igneous rocks.

Microcline and *sanidine* are polymorphs, where the Si and Al atoms being randomly distributed over their lattice positions in *sanidine* but ordered in *microcline*, generally the rapid crystallization prevents the attainment of an ordered arrangement of Si and Al.

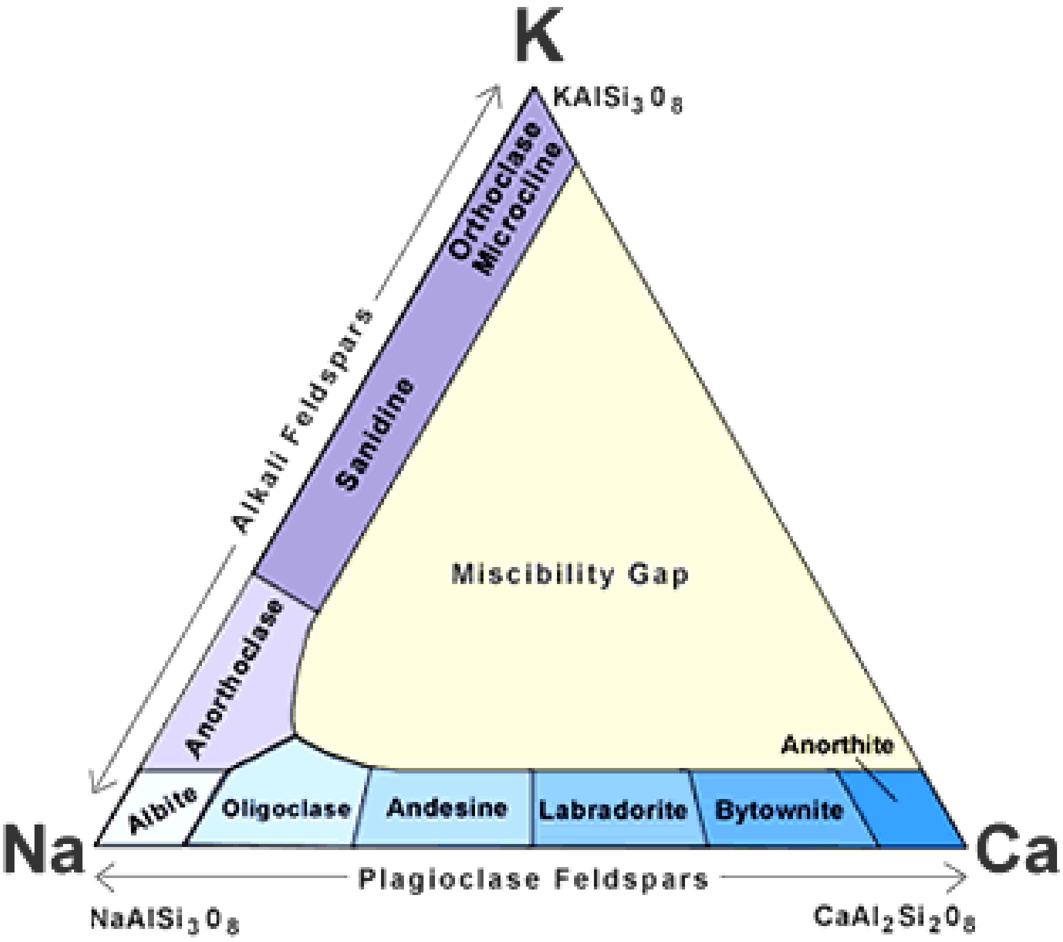
At the high temperature complete solid solution exists between $KAlSi_3O_8$ (**orthoclase**) and $NaAlSi_3O_8$ (**albite**), the more potassic members are called ***soda-orthoclase***, and the more sodic members are called ***anorthoclase***.

At lower temperature solid solutions intermediate between ***albite*** and ***orthoclase*** are metastable and under conditions of slow cooling, they break down into an oriented intergrowth of sub parallel lamellae, alternately sodic and potassic in composition, such an intergrowth is called **perthite**.

In the **perthite** the plagioclase occurs as oriented veins or patches within the orthoclase (or microcline); in the **antiperthite** this relation is reversed.

At high temperatures the **K** and **Na** ions are distributed in framework producing a homogeneous crystal, but at lower temperatures ordering may occur with formation of potassium-rich and sodium-rich lamellae, producing alternate sheets.

Nearly all ***perthites*** have been formed by **exsolutions** (the process whereby an initially homogeneous solid solution separates into two or more phases without addition or removal of material, i.e., without change in the bulk composition).



Plagioclase feldspars are a very important group of igneous rock forming minerals. Plagioclase comprises a solid solution series: $NaAlSi_3O_8$ (**Albite**)- $CaAl_2Si_2O_8$ (**Anorthite**).

Plagioclase feldspars range between two end members: the sodic feldspar end member albite and the calcic feldspar end member anorthite.

The composition of plagioclase feldspar is typically determined by the percentage of anorthite (An%) in system. The members of this series are known as the sodic-lime feldspars, and as a group are called the plagioclase feldspars.

There are four intermediate plagioclase feldspars that are recognized between albite and anorthite based on the An%.

Plagioclase feldspars exhibit features similar to those of alkali feldspars, but in most cases the features are more complicated.

The compositions of the different plagioclase feldspars in terms of An%, as well as the percentage of albite in the system, well expresses as the following:

- **Albite** (0-10% anorthite) is found mostly in very Na-rich environments.
- **Oligoclase** (10-30% anorthite) is the principal plagioclase in granitic rocks.
- **Andesine** (30-50% anorthite) is the principal plagioclase in intermediate rocks.
- **Labradorite** (50-70% anorthite) is the principal plagioclase in gabbroic rocks.
- **Bytownite** (70-90% anorthite) is the least common plagioclase. It is too calcic to form from most magma. It is the first feldspar to form in mafic magmas and may be present in the cores of zoned feldspars.
- **Anorthite** (90-100% anorthite) is too calcic to form magmatically and forms mostly from metamorphism of calc-silicate rocks.

Chemical variations in the mica minerals

A general formula for all members of the mica group can be writing as; $W\ (X\ Y)_{2-3}\ Z_4O_{10}\ (OH, F)_2$. In this formula ***W*** is nearly potassium (Na in paragonite); ***X*** and ***Y*** represent Al, Li, Mg, Fe^{2+} and Fe^{3+}; ***Z*** represents Si and Al. The members of the mica group may be as the following:

Muscovite	$K\ Al_2\ (Al\ Si_3O_{10})\ (OH)_2$
Paragonite	$Na\ Al_2\ (Al\ Si_3O_{10})\ (OH)_2$
Phlogopite	$K\ Mg_2\ (Al\ Si_3O_{10})\ (OH)_2$
Biotite	$K\ (Mg, Fe)_3\ (Al\ Si_3O_{10})\ (OH)_2$
Lepidolite	$K\ Li_2\ Al\ (Si_4O_{10})\ (OH)_2$

In the structural scheme of mica, the SiO_4 tetrahedra is linked by three corners to neighbouring tetrahedral forming sheet, and each SiO_4 tetrahedra has one free oxygen. These sheets to form bounded double sheets, they are cross-linked by **Al** in muscovite or by **Mg** and **Fe** in phlogopite and biotite, also (OH) group is incorporated and linked to Al, Mg, or Fe. The structure is a succession of such double sheets, with the potassium ions placed between them.

Generally 28 known minerals of the mica group, but only **5** are common rock-forming minerals. **Muscovite**, the common light-coloured mica, and **biotite**, which is typically black, are the most abundant. **Phlogopite** is typically brown. **Lepidolite**, generally pinkish in colour, occurs in lithium-bearing pegmatites.

All of these micas exhibit easily observable perfect cleavage into flexible sheets.

The common mica of igneous rocks is biotite. Muscovite is present in some granites.

Phlogopite is sometimes found in igneous rocks rich in magnesium and poor in iron. Paragonite is a rare mineral of schist.

What are the significances of chemical composition of Biotites in igneous rock chemistry?

Biotites from igneous rocks are variable in chemical composition. Part of the hydroxyl may be replaced by fluorine. Minor amounts of Mn, Ti, Li, Na, and Ca are recorded in analyses of biotite.

There is a general trend from magnesium-rich biotites in intermediate igneous rocks to iron-rich biotites in granites and syenites.

Aluminum is greater in biotites from pegmatites and **Al** is lowest in biotites from intermediate and basic igneous rocks.

Biotite is a significant ferromagnesian minerals in most intermediate and felsic igneous rocks, and also occurs as minor phase in some mafic rocks.

Biotite shows the nature physicochemical conditions of magmas from it formed.

In biotite chemistry there are considerable sensitive parameters, which they use to construct very useful discrimination diagrams, which are helpful in understanding the nature physicochemical conditions of magmas.

The chemical composition of biotite minerals representing three magmatic groups and related rocks as :

1) Biotite in anorogenic extensional-related alkaline rocks
2) Biotite in calc-alkaline I-type orogenic granites
3) Biotite in peraluminous rocks including collisional and S-type granites

Biotites in **alkaline anorogenic** suites are typically iron-rich and the ratio of **FeO /** MgO = about **7 and** associated with alkali amphibole, alkali pyroxene

Biotites in **calc-alkaline suites** are moderately **enriched in Mg** (**FeO/**MgO = about **2**), and are typically associated with calcic pyroxene and/or calcic amphibole

Biotites in **peraluminous** suites (including S-type) are rich in **Al** and the ratio of **FeO /** MgO = about **3.5**

Chemical variations in the feldspathoids

The feldspathoids are a group of alkali-aluminum silicates, which appear in place of the feldspars when an alkali-rich magma is deficient. They are never associated with primary quartz. The following minerals are the more important members of this group:

Leucite	$KAlSi_2O_6$	Sodalite	$Na_8Al_6Si_6O_{24}(Cl_2)$
Kaliophilite	$KAlSiO_4$	**Nepheline**	$NaAlSiO_4$
Kalsilite	$KAlSiO_4$	Noselite	$Na_8Al_6Si_6O_{24}(SO_4)$
		Cancrinite	$Na_8Al_6Si_6O_{24}(HCO_3)_2$

The feldspathoids are not homogeneous series like the feldspars or the pyroxenes. The SiO_4 and AlO_4 tetrahedra are linked as the feldspars, whereas the metal ions fit into cavities in the framework.

Nepheline and **Leucite** are the commonest of the feldspathoids. Leucite is the commonest potassium feldspathoid. It is abundant in the volcanic rocks of a few regions. It is not found in plultonic rocks. Leucite is not a stable phase in the K_2O-Al_2O_3-SiO_2 system **at high pressures.** Analyses of leucite show that a little sodium may replace potassium in the structure.

Nepheline is found in both plutonic rocks and sometimes in volcanic rocks. Nepheline always contains some potassium replacing sodium, the Na:K ratio often being close to 3 : 1

Geochemical Instrumentation and Mineral Analysis

No matter what process is involved, a particular mineral cannot form unless the chemical components necessary to make the mineral are present. Thus, the most common minerals are minerals that have a chemical composition made of the common elements found in their environment.

Methods of Chemical Analysis

While the common minerals are made up mostly of the abundant elements in the crust, and we can express the chemical composition of such minerals by a simple chemical formula (and sometimes not so simple), all minerals exhibit some chemical variation. In fact pure minerals (those with a chemical composition exactly the same as the chemical formula) are rarely found in nature.

Various methods have been used to perform chemical analyses of rocks and minerals. But, analysis of minerals is quite different from analysis of rocks. Chemical analysis of rocks involves analyzing an aggregate of minerals.

Analysis of a mineral is more complicated than analysis of rocks because:-

1. Individual minerals are much smaller than rocks and it is therefore difficult to obtain enough sample of a mineral to perform the chemical analysis.

2. The single mineral is too small to provide enough sample, so several grains of the same mineral can be separated from a rock and analyzed as a single sample. But, this involves extensive work in separating the mineral form all other minerals, and still does not tell us if there is any chemical variability between individual grains. (The electron microprobe technique described below is an exception, because it allows for analysis of small areas of single grains).

3. Individual minerals may be chemically zoned, so may be differences in the chemical composition of the mineral from its center to its rim. Chemical analysis of single mineral grains or aggregates of mineral grains will not reveal this chemical zoning. (Again, the electron microprobe technique is an exception).

Here we discuss briefly the more commonly used method of mineral analysis.

Electron probe micro-analyzer (EPMA)

What is Electron probe micro-analyzer (EPMA)

EPMA is also called an **electron microprobe**, or just **probe**. An electron microprobe is a high powered microscope that uses electrons, rather than light, to examine a rock sample.

Because electrons are charged particles, they can be accelerated towards, and focused on a sample surface.

The electron microprobe is an instrument that uses principles similar to XRF, but the main difference an electron beam is used.

The importance of an **EPMA** is the ability to acquire quantitative elemental analyses at very small sizes of about 1 µm (1µm = 10^{-6}m).

EPMA has the ability to measure the concentrations in small parts of mineral grains, and chemical zoning patterns or changes in the concentration of elements through an individual grain.

Also the importance of an **EPMA** is the ability to create **detailed images** of the sample and to resolve complex chemical variation within single phase.

The electron (EPMA) optics allow much higher resolution images than can be seen using visible-light optics, so you can be to study detailed micro textures**.**

Preparation of microprobe sample

Analysis by EPMA need samples to be polished, either as circular blocks or thin sections, and carbon coated.

Samples that need to be prepared (cut, mounted and polished) should be presented to the preparation laboratory at least two weeks prior to the Cameca SX100 booking.

A brief protocol for preparation of microprobe sample is provided here:

1. Samples are prepared as standard-size 27 x 46 mm rectangular sections, or in 1-inch round disks.
2. Sections of rocks are most often prepared as 30-micron-thick sections without cover slips.
3. Chips can be mounted in epoxy disks, and then polished to expose a cross-section of the material.

4. Prior to analysis, the sample must be having a fine **polish** - and **coated** with a thin film of **carbon**.
5. Samples are loaded into the sample chamber and mounted on the sample stage.
6. To begin a microprobe session, suitable analytical conditions must be selected, such as accelerating voltage and electron beam current, and the electron beam must be focused.
7. If quantitative analyses are planned, the instrument first must be standardized for the elements desired.

How does electron microprobe instrument work?

1) Before starting a microprobe session, it is best to have an analytical plan in mind based on petrographic observation, so that one has a good idea of what phases to analyze in the samples of interest.
2) The microprobe instrument consists of a large tank to produce a vacuum.
3) At the top is an electron gun that has a filament, similar to that in an X-ray tube that generates electrons.
4) The electron beam is accelerated down to a sample stage that is moveable.
5) The electron beam is focused to a diameter of about **1μm**. Because the electrons are charged particles, so they can be focused using electronstatic lenses.

6) Most electron microprobes have at least **3** X-ray spectrometers inside, so that more than one element can be measured at once.

7) A microscope with binocular allows the user to focus the electron beam anywhere on the sample.

8) Electrons striking the small area of the sample will produce X-rays with wavelengths characteristic of the elements in the sample (interaction between the electron beam and the sample produces characteristic X-rays, that have a wavelength and energy proportional to the atom of the element from which they are produced).

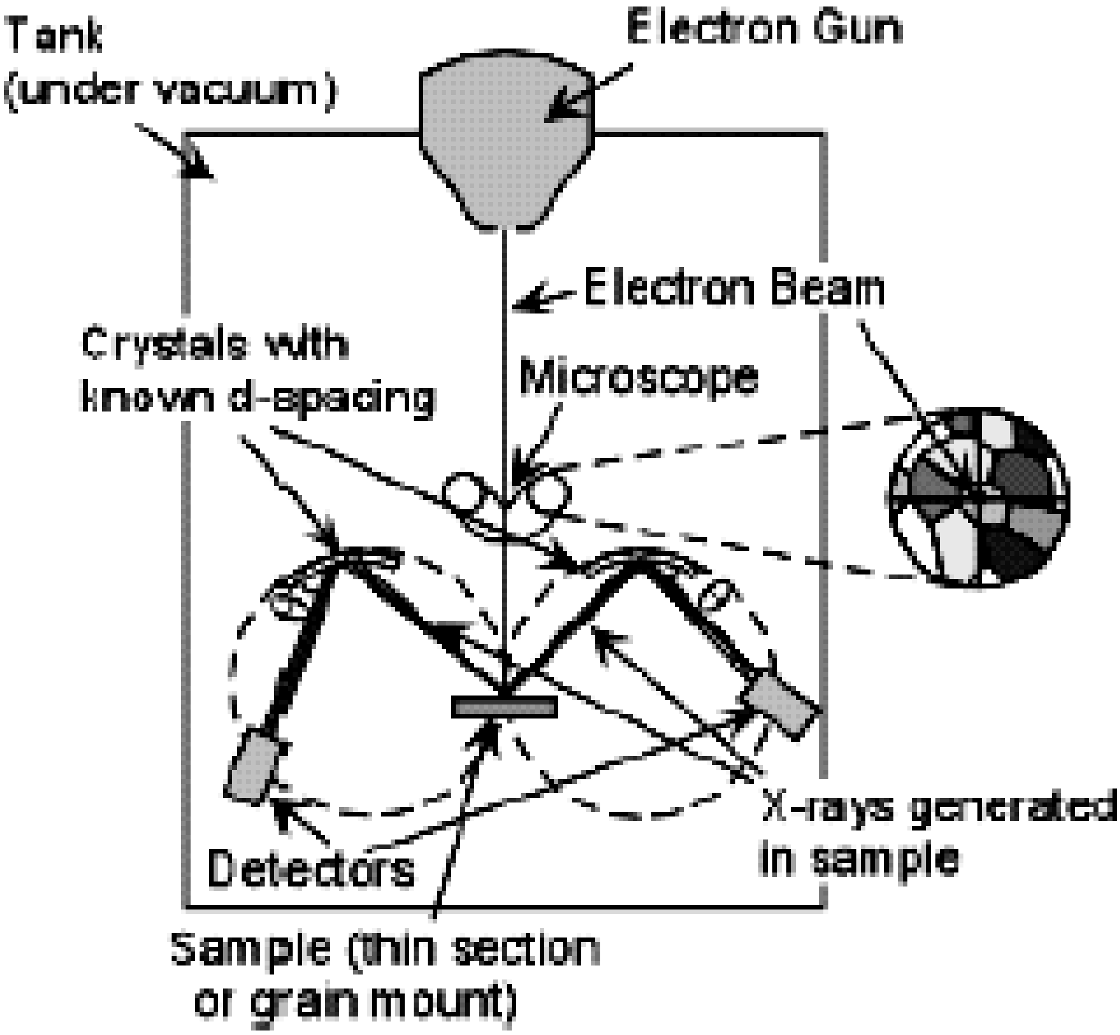
9) The spectrometers consist of curved crystals of known **d-spacing**. These spectrometers diffract X-rays of each element into the detectors.

10) Several elements can be measured at once.

11) Data output (after standardization, and data correction) is typically a data of weight percent of the simple oxides.

12) The compositional data can be recalculated as mineral structural formulae.

13) Electron microprobe analysis is useful for determining the major element concentration, but it is much less sensitive for determining trace element concentrations.



The strengths of the electron microprobe

1) An electron microprobe is that enable quantitative chemical analysis at high sensitivity.
2) An electron microprobe is the tool for chemical analysis of minerals at small scales (1-2 micron diameter); so, the user can analyze minute phases in a rock.
3) An electron microprobe produces chemical analyses allow the user to detect small compositional variations and chemical zoning within the crystals of minerals.

4) Electron probes allow the investigator to generate images of the internal compositional structures within minerals.

5) Microprobe analyses are reported as oxides of elements, not as cations; therefore, cation proportions and mineral formulae must be recalculated

Geochemistry of igneous rocks

Igneous rocks are classified on basis of:

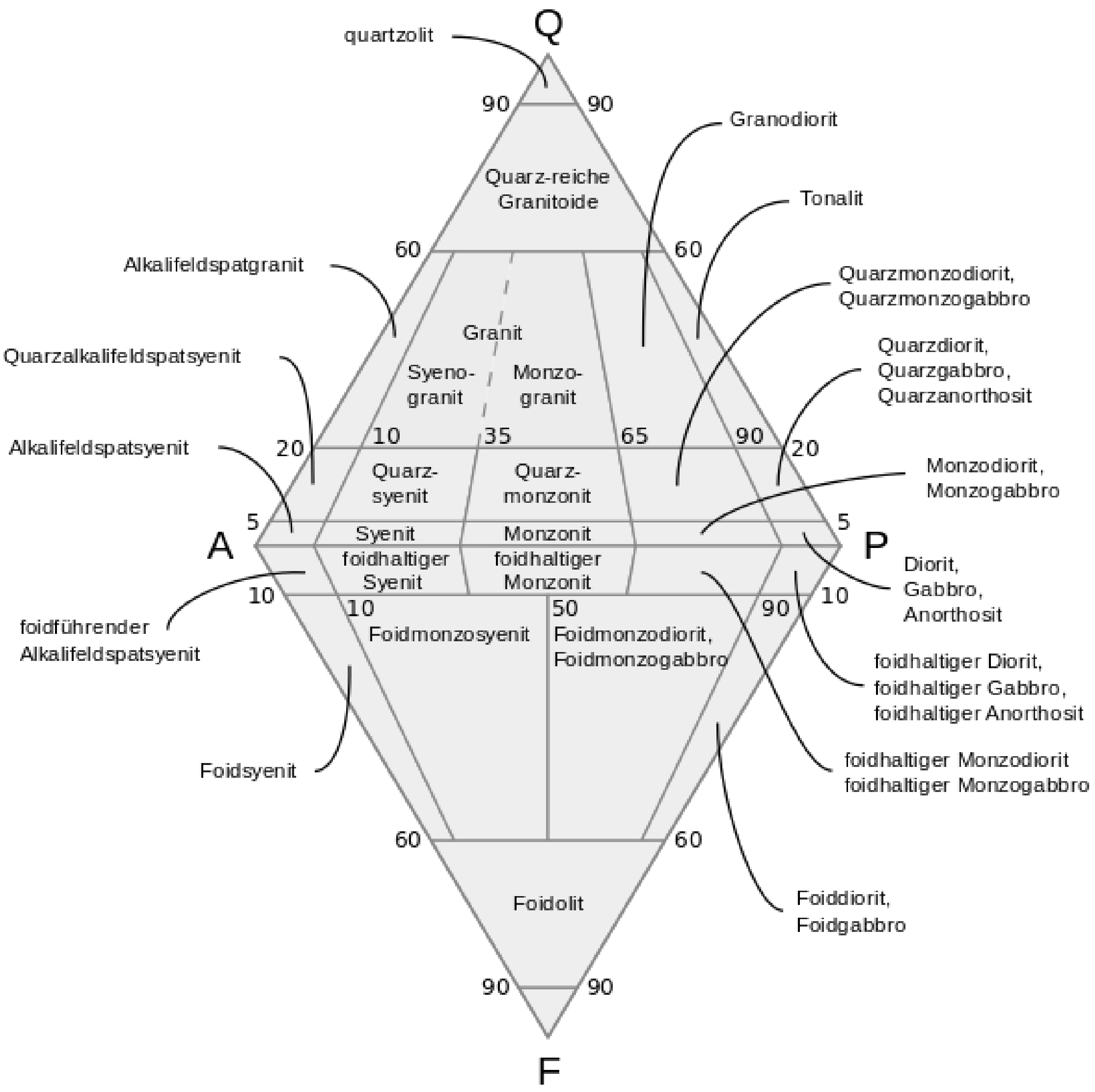
1. **Structural and field relationships**
2. **Mineral and modal composition (Modal analysis)**
3. **Bulk chemical composition**

2-Modal analysis - requires only a thin section. Modal analysis produces an accurate representation of the distribution and volume percent of the mineral within a thin section. Modal analysis can be used to compare rocks from different areas if you only have thin sections.

Modal classification of plutonic and volcanic rocks is based on relative volume proportions of mineral groups. Modal analysis plot on **QAPF** diagram in which the minerals are grouped into four individual groups:

Q – quartz, tridymite, **A** – alkali feldspars (orthoclase, microcline,….)

P – plagioclase **F** – foids (nepheline, leucite, ,…..).



Modal QAPF classification of plutonic rocks (Streckeisen 1976)

QAPF diagram is used to classify plutonic rocks. Although similar diagram exists for volcanic rocks, volcanic rocks are typically too fine-grained for mineralogical analysis, so they are classified according to their chemistry and TAS diagram is used instead of QAPF diagram.

3- Bulk rock chemical composition

The chemical composition of igneous rocks depend on:-

- **a)** The composition of the source material
- **b)** Depth of melting
- **c)** Secondary alteration and tectonic environment
- **d)** Where does crystallization of igneous rocks occur?

Geochemical data are subdivided into four main categories:-

1) Major elements data
2) Trace elements data
3) Radiogenic isotopes data
4) Stable isotopes data

There are several classification schemes based on bulk chemical composition, employing either the chemical composition expressed in wt. % or the normative composition expressed in mol. %. These classification schemes are used for fine grained rocks, for which determination of modal composition is impossible (aphanitic volcanic rocks) and can be used also for phaneritic rocks, in which the modal composition reflects the origin and evolution of parental magma.

The major elements are the elements which predominate in the rock analysis. They are accompanied by an appropriate amount of oxygen, so their concentrations are expressed as a weight percent (wt %) of the oxides. They are the 13 major oxide components which are reported as weight percent (wt%).

Major Elements as Oxides	
Oxide	***Range in normal igneous rocks***
SiO_2	35 - 80 wt%
Al_2O_3	8 - 22 wt%
TiO_2, Fe_2O_3 (ferric), FeO (ferrous), MnO, MgO, CaO	4 - 30 wt%
Na_2O	1.5 - 6 wt%
K_2O	0.5 - 8 wt%
H_2O	Varies
P_2O_5	< 0.15 wt%
CO_2	Varies

The sum of the major element oxides **will total to about 100%.** Iron may be determined as FeO and Fe_2O_3, but is sometimes expressed as (total **Fe**) and given as **FeO_{total}**.

TiO_2 and H_2O are sometimes included in the major elements analysis. Water combine within the lattice of silicate minerals and driven off by heating the rock powder below 110° C.

Trace elements are defined as those elements which are present at less than the 1%, and their concentrations are expressed in part per million (ppm). These elements include: Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga ,Rb, Sr, Y, Zr, Nb Ba, Pb plus F, Cl,. Rare Earth Elements (REE or lathanides atomic number 57 to 71) are reported in ppm or mg/g. The REE are important for petrogenetic studies. Theoretically any element can be analyzed, but you must be aware of the overall composition of the rock, e.g. basalt - analyze for Cr, Ni, Cu, but not for Li, Ba, because these are not important or necessary to analyze for as they are not present in detectable amounts, where granite pegmatite with lepidolite mica, analyze for Li, and Ba but not Cr, Ni, Cu.

Isotopes are subdivided into radiogenic and stable isotopes. Radiogenic isotopes include those isotopes which decay spontaneously due to their natural radioactivity and those which are the final daughter products of such a decay scheme. They include the parent- daughter element pairs Rb-Sr, Sm-Nd, U-Pb and K-Ar. They are expressed as ratios either in absolute terms ^{87}Sr/ ^{86}Sr or relative to a standard. Stable isotopes include H, O and C.

Using major element data in geochemistry of igneous rocks

The discussion will be restricted to the **10** elements traditionally listed as oxides in major element chemical analysis; Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K and P.

Geochemistry makes use of major element data in three principal ways:

A- In rock classification and nomenclature.

B- In the construction of variation diagrams.

C- In the identification of the original tectonic setting of igneous rocks.

Using of major element chemistry in classification and nomenclature of igneous rocks

The application of major element chemistry to rock classification and nomenclature is widely used in igneous rock geochemistry. XRF analysis is very useful in some cases to classify igneous rocks on the base of their chemical composition.

The chemical classification schemes of igneous rocks described as the following:

1-Oxide-oxide plots

The total alkalis-silica diagram (TAS)

2-Norm based classification

- granite classification using the Ab-An-Or diagram
- basalt classification using the Ne-Di-Ol-Q diagram

3-Cation classifications

volcanic and plutonic rocks using $\mathbf{R_1}$ and $\mathbf{R_2}$

1 - Classification of igneous rocks using oxide-oxide plots

The total alkalis-silica diagram (TAS)

TAS is one of the most useful classification schemes for volcanic rocks. Chemical data as the sum of $\mathbf{Na_2O}$ and $\mathbf{K_2O}$ content (total alkalis, TA) and the SiO_2 (S) are directly from rock analysis as wt% oxides and plotted onto the classification diagram.

If the analysis falls in certain fields, additional calculations, such as the CIPW norm, must be performed in order to arrive at the correct root name of the rock.

The **TAS** classification was originally constructed with the more common rock types using the following principles:-

(**a**) Each field was chosen to accord as closely as possible with the current usage of the root name with the help of data from 24,000 analyses of fresh volcanic rocks from the CLAIR and PETROS databases (**Le Maitre, 1982).**

(**b**) Fresh rocks were taken to be those in which $H_2O < 2\%$

(**c**) Each analysis was recalculated to 100%

(**d**) Boundaries between fields were located to minimize overlap between adjacent fields.

The **TAS** diagram was demonstrated by Cox et al., (1979), who showed that there are theoretical reasons for choosing Si_2O and $Na_2O + K_2O$ as basis for the classification of volcanic rocks. The current version of the diagram after Le Bas et al, (1986) (Fig. 3)

The **TAS** diagram divides rocks into ultrabasic, basic, intermediate and acid on the basis of their silica content.

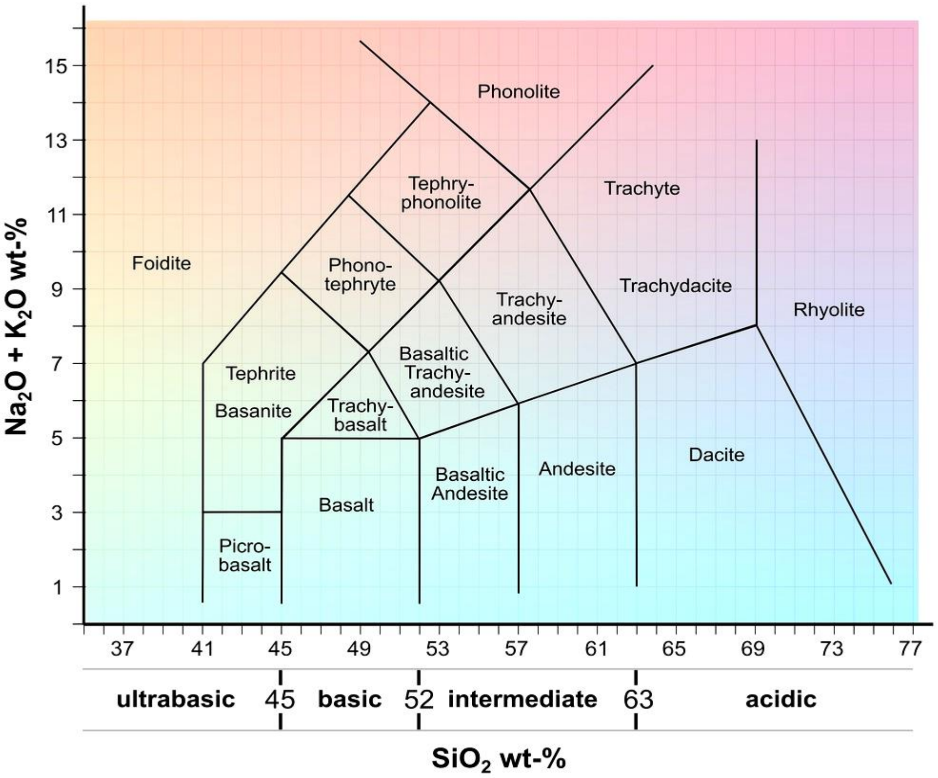


Fig. 3: Total alkalis versus silica chemical classification diagram (Le Bas et al, 1986) for volcanic rocks

The TAS classification scheme is intended for the common fresh volcanic rocks.

The TAS classification is inappropriate for potash-rich rocks and highly magnesian rocks and should not be normally used with weathered, altered or metamorphosed volcanic rocks because the alkalis are likely to be mobilized.

2- Classifying of igneous rocks using the norm

The norm calculation is a way of working out the mineralogy of a rock from a chemical analysis.

Normative analysis is defined as the calculation of a theoretical assemblage of standard minerals for a rock based on the whole rock chemical composition as determined by analytical techniques and the norm of a rock may be substantially different from the observed mineralogy.

The original purpose for the norm was essentially taxonomic. An elaborate classification scheme based on the normative mineral percentages was proposed.

Various types of **NORM**s have been proposed as CIPW, Niggli. The CIPW norm is the most commonly used calculation scheme

The CIPW norm, originally proposed in 1919, was proposed as a means of comparing and classifying all igneous rocks for which chemical analyses were available. The NORM takes its name from the four authors who proposed it - **C**ross, **I**ddings, **P**irsson and **W**ashington. This NORM was very elegant and **based on a number of simplifications**:

1. The feromagnesium minerals are assumed to be free of $\mathbf{Al_2O_3}$.
2. The **Fe/Mg** ratio for all feromagnesium minerals is assumed to be the same.
3. Several minerals are assumed to be incompatible, thus nepheline and/or olivine never appear with quartz in the norm.

The CIPW norm calculations are normally made by computer, and there are various published programs for the calculation of the CIPW.

In the CIPW norm calculation, the rock chemistry is converted to molecular proportions by dividing the wt% oxides by their molecular weight, and at the end of the calculation the proportions of normative minerals are react as wt% by multiplying by the molecular weight. This is known as the wt% norm.

Streckeisen and Le Maitre (1979) proposed a classification diagram for plutonic rocks (Fig. 7) based upon their normative composition, which was intended to mirror the Streckeisen QAPF classification.

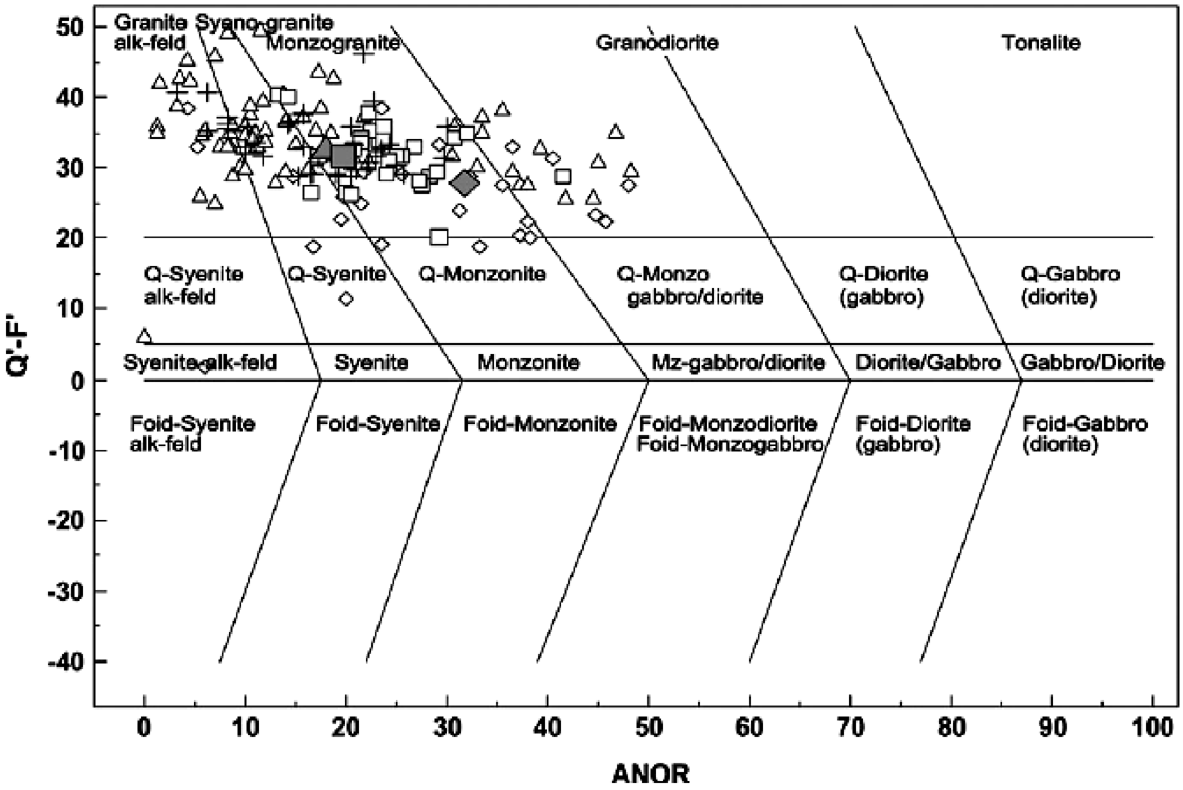


Fig. 7: The classification of plutonic rocks using their normative compositions after Streckeisen and Le Maitre (1979)

The diagram has rectangular coordinates of which the y-axis reflects the degree of silica saturation and is either is a measure of quartz content, where **Q`**= (Q/Q+Or+Ab+An)*100 and **F`**= (Ne + Le)/ (Ne + Le + Or + Ab + An). The x-axis reflects changing of feldspar composition **ANOR**= An /(Or + An)*100

The Ab-An-Or classification diagram

It can be applied to felsic rocks with more than 10% normative quartz. The diagram (Fig. 8) is based upon the **normative feldspar** composition react to 100%.

The **Ab –An -Or** classification diagram has been chiefly used to classify plutonic rocks although **Connor (1965)** intended his classification to be used with both volcanic and plutonic felsic rocks and **Barker (1979**) has proposed a modification to the diagram, slightly expanding the field of **trondhjemite** (**trondhjemite** is a variety of tonalite in which the plagioclase is mostly in the form of sodic plagioclase with an oligoclase composition. Trondhjemite is sometimes known as plagiogranite). The diagram can also be used with deformed and metamorphosed granitic rocks.

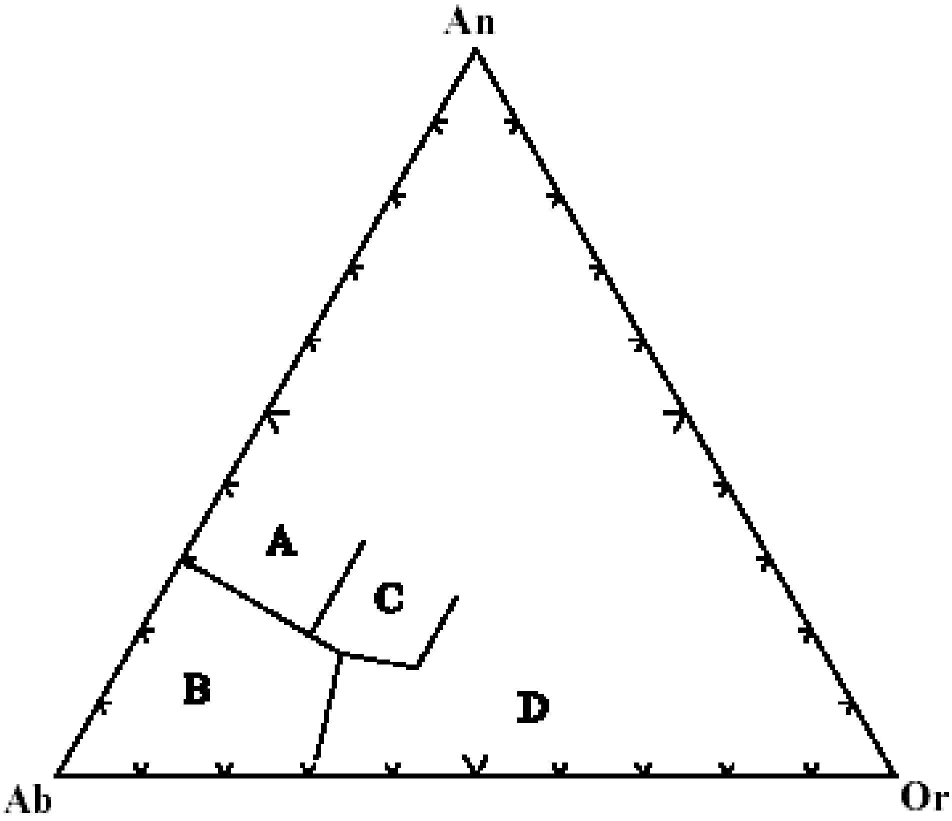


Fig.8: Normative albite-anorthite-orthoclase triangular diagram(Barker, 1979), for the classification of plutonic felsic rocks.
A:Tonalite ; B:Trondhjemite ; C:Granodiorite ; D:Granite

Thompson (1984) proposed a classification scheme for basalts based upon their CIPW normative proportions of nepheline (and other feldspathoids), olivine, diopside, hypersthene and quartz. This diagram is shown in Fig. 10. The three equilateral triangles of this diagram Ne-Ol-Di, Ol-Di-Hy and Di-Hy-Q represent basaltic and related rocks which are respectively undersaturated, saturated and oversaturated with silica.

The silica-undersaturated basalts (alkali basalt) are characterized by normative olivine and nepheline.

Silica- saturated basalts (olivine tholeiites) are characterized by normative olivine and hypersthene,

Silica- oversaturated basalts (quartz tholeiites) are characterized by normative quartz and hypersthene.

Silica- saturation is important in basaltic magmas, because in dry magmas this single parameter determines the crystallization sequence of minerals and direction of evolution during fractional crystallization.

The Thompson (1984) diagram should not be used for highly evolved magmas and best applied to basalts which have more than 6% MgO.

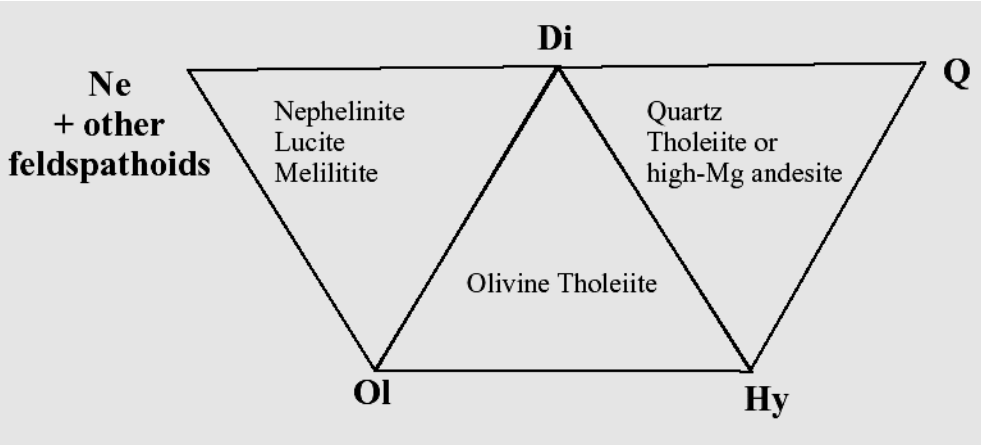


Fig. 10: The classification of basic and ultrabasic magmatic rocks using their CIPW normative compositions after Thompson (1984)

3- Classifying of igneous rock using cations

In order to that, wt% oxide data do not faithfully reflect the cation distribution of a sample, so numbers of authors prefer to recalculate the rock composition as cations.

In classifying of igneous rock using cations, the wt% oxide is divided by the molecular weight of the oxide and multiplied by the number of cations in the formula unit.

In order to calculation the proportion of **Si**, the wt% Si_2O is divided by **60** and multiplied by 2, however in order to calculation the proportion of **Al**, the wt% Al_2O_3 is divided by **101** and multiplied by 2. In some cases the cationic proportions are multiplied by 1000 and described as millications.

De La Roche et al., (1980) proposed a classification scheme (Fig.11) for volcanic and plutonic igneous rocks based upon their cationic proportions, expressed as millications.

De La Roche et al., (1980) diagram based upon the plotting parameters R1 and R2.

R1=4Si -11(Na + K) - 2(Fe +Ti); **R2** = 6Ca + 2Mg + Al

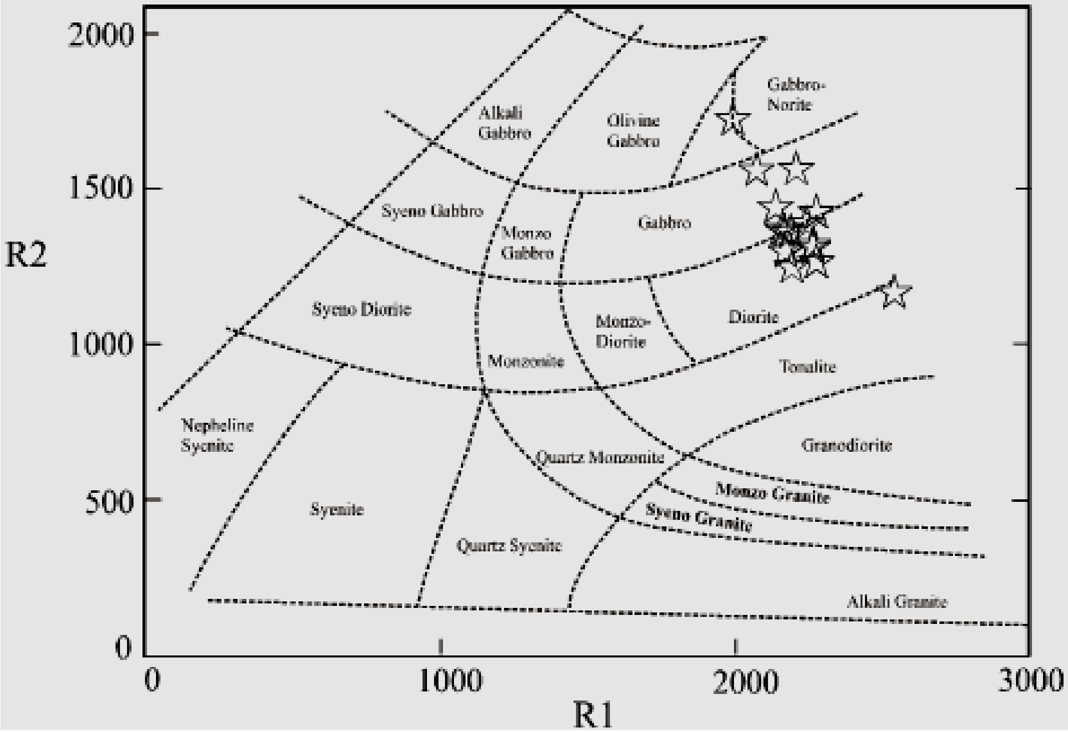


Fig.11: ***R1 - R2 classification diagram for plutonic igneous rocks (de La Roche, 1980).***

The **Jensen** cation plot is classification scheme for subalkaline volcanic rocks. It based upon the proportion of the (Fe^{3+} + Fe^{2+} + Ti), Al and Mg recalculated to 100% and plotted on a diagram (Fig.12).

Classification scheme can be used successfully with metamorphosed volcanic rocks, which have suffered mild metasomatic loss of alkalis. The main important of this diagram, however, is that it shows **komatiite** clearly as a separate field from basalts and from calc-alkaline rocks (***Komatiite*** *is an ultramafic, high-magnesian volcanic rock typical originated during fast cooling of a magma enriched in olivine and other Mg-Fe silicate minerals. with high MgO contents; 18-30 wt. %*).

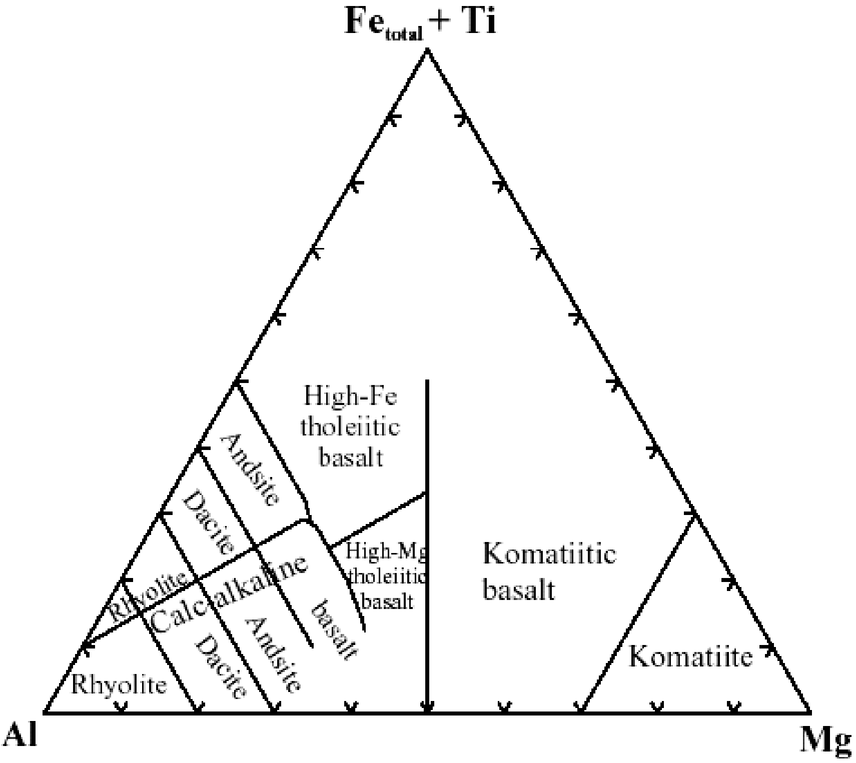


Fig.12: The classification of volcanic rocks using their cation percentages of (Fe_{titalv}+Ti), Al and Mg after Jensen (1976).

Variation diagrams

A main objective of any research program on igneous rocks is to describe and display chemical variations for simplicity and to facilitate condensing information. The best way to simplify and condense analytical data is by graphical means.

Harker Diagrams

The oldest method is the variation diagram or Harker diagram, which dates from 1909. Any element or oxide which exhibits a wide variation in abundance may be chosen as the abscissa (X- axis) resulting in a similar set of diagrams, however individual analysis would not appear in the same sequence on each diagram. **SiO_2** is generally chosen as the plotting parameter for many igneous rock series on the variation diagrams, however, the fact that SiO_2 is the most abundant oxide in igneous rocks and exhibits a wide variation in composition, and then plots oxides of elements against SiO_2.

Harker diagram graphical presentation is useful for large quantities of analytical data and yields an approximation of inter-element variations for a group of rock samples.

The following plots (Fig.13) present chemical data for a suite of plutonic rocks. With increasing silica the following trends are evident:

1. Al_2O_3, Fe_2O_3, MgO and CaO decrease in abundance with increasing silica.
2. K_2O and Na_2O increase with increasing silica.

A genetic link can be inferred from these Harker diagrams, i.e. that the lowest SiO_2 content present on the diagram represents the original or first liquid, for the group of samples presented, from which all other liquids were derived.

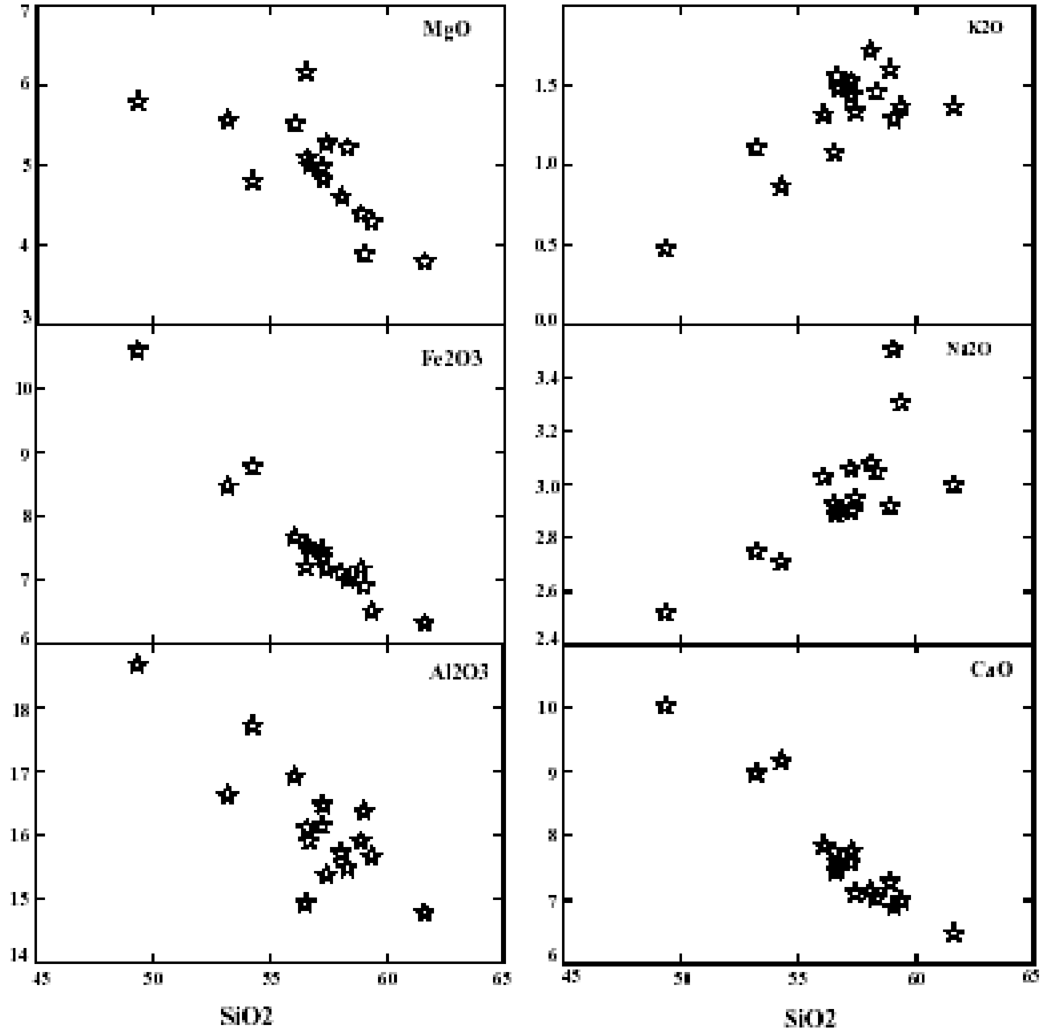


Fig.13

One of the most commonly used alternatives to Harker diagram is MgO plot on the X-axis. This is appropriate for rock series which include abundant mafic members, for in this case the range of SiO_2 concentrations may be small, on the other hand MgO is an important component of the solid phases in equilibrium with mafic melts and shows a great deal of variation.

Triangular variation diagrams are used when it is necessary to show simultaneous change between three variables.

The **AFM diagram** is the most popular of triangular variation diagrams and takes its name from the oxides plotted at its apices. Alkali ($Na_2O + K_2O$), Fe oxides ($FeO+Fe_2O_3$) and MgO

Most authors use oxide wt% when plotting data on an **AFM** diagram but in few cases atomic proportions are used. The shape of the trend is similar in each case but the position of the atomic proportions plot is shifted away from the **Fe** apex relative to the position of the oxide plot for the same data. The

AFM diagram is most commonly used to distinguish between **tholeiitic** and **cal-alkaline** differentiation trends in the subalkaline magma series and shows the following:-

A) ***Tholeiitic trend*** is marked by iron enrichment caused by crystallization of olivine and pyroxene. The Fe enrichment is then followed by late swing toward alkalis. Tholeiitic trends occur mostly in *island arcs*.

B) ***Calc-alkaline trend*** exhibits ***small amount of iron enrichmen***t during differentiation, this is because of the crystallization of amphibole, which has approximately the same Mg/Fe ratio as the coexisting melt.

The calc-alkaline series generally has more H_2O than the tholeiitic series. Calc-alkaline series are dominant in *andesitic-type* subduction zones.

Irvine and Baragar (1971) present dividing lines separating the rocks of the cal-alkaline series and rocks of the tholeiite series (Fig.14)

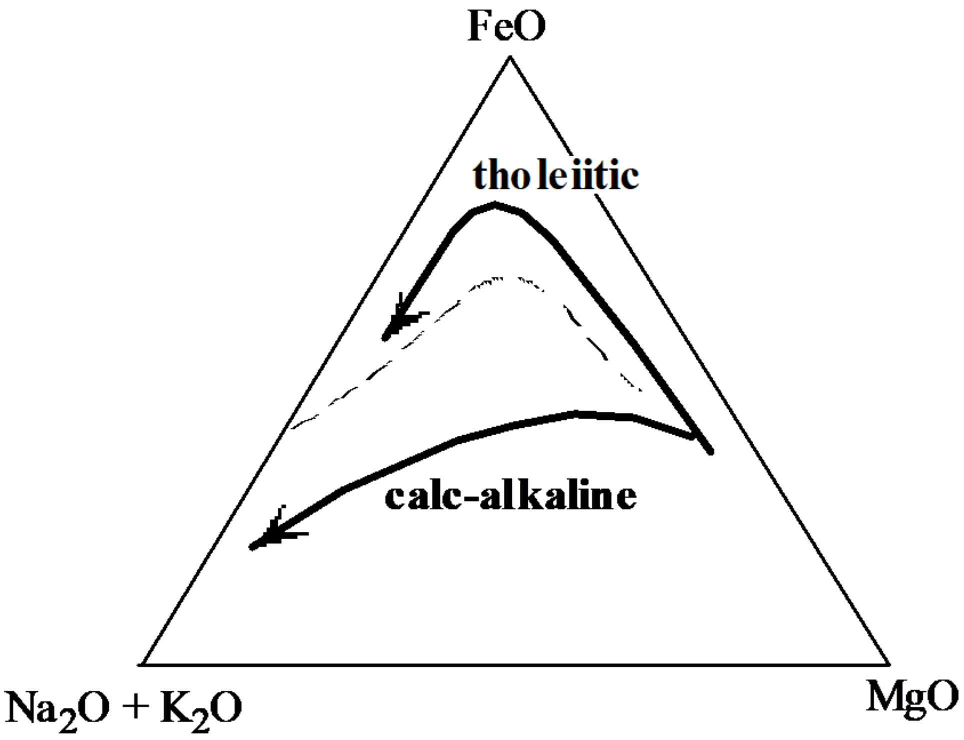


Fig. 14: AFM diagram after Irvine and Baragar (1971)

AFM ternary diagram has been also used to differentiate between **compressional** and **extensional** suites (Petro *et al*, 1979). The **extensional** trend runs close and nearly **parallel to the AF** - side at compositions approaching the alkali apex, while the **compressional** trend tends to be nearly perpendicular to the FM - side.

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