CHAPTER: III

III. Minerals of igneous rocks and their order of appearance

III.1 Introduction

The mineralogical composition of igneous rocks is **a function of the chemical composition of the magma and its crystallization conditions**.

The minerals that constitute more than 99% of igneous rocks belong to 8 groups of minerals (mainly silicates and aluminosilicates): quartz, feldspars, feldspathoids, olivines, pyroxenes, amphiboles, biotites (micas), iron oxides

The chemical composition of igneous rocks is represented in the form of oxides (major, minor elements) and on the basis of the SiO2 content we distinguish the following groups:

- Acidic rocks: > 66% SiO_2
- Intermediate rocks: 52 to 66% SiO_2
- Basic rocks (mafic): 45 to 52% SiO_2
- Ultrabasic rocks (ultramafic): ≤45% SiO_2

The essential minerals of igneous rocks belong to the silicate class:

- ✓ Quartz
- ✓ Feldspars: orthoclase $KAlSi_3O_8$- albite $NaAlSi_3O_8$ – anorthite $CaAl_2Si_2O_8$
- ✓ Feldspathoids: nepheline $Na_3K(AlSiO_4)_4$ – leucite $KAlSi_2O_6$
- ✓ Micas: muscovite $KAl_2(AlSi_3O_{10})(OH)_2$ – biotite $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$
- ✓ Olivine $(Mg,Fe)_2SiO_4$
- ✓ Pyroxenes
- ✓ Amphiboles

Quartz, Feldspars, Feldspathoids = **Felsic minerals**

Olivine, Biotite, Pyroxenes, Amphiboles = **Mafic minerals**

+ **accessory minerals** such as **Apatite** $Ca_5(PO_4)_3(OH,F,Cl)$, **Ilmenite** $FeTiO_3$,

Magnetite Fe_3O_4, **Zircon** $ZrSiO_4$, **Sphene** $CaTiSiO_5$

Based on the volume percentage of mafic minerals, igneous rocks are classified into three categories:

• **leucocratic** (0 to 30%);

• **mesocratic** (30 to 60%);

• **melanocratic** (60 to 100%).

III.2. The minerals of igneous rocks belong to the silicate class:

III.2.1. Quartz:

Quartz (silica, SiO_2) represents about 12% of all minerals in igneous rocks. It is the characteristic mineral of acidic rocks; it is poorly represented in intermediate rocks and absent in basic rocks.

Quartz belongs to the tectosilicate family. It has six polymorphic varieties, each crystallizing under well-defined pressure and temperature conditions (Figure 1): α-quartz, β-quartz, tridymite, cristobalite, coesite, and stishovite. The quartz stable to the temperature and pressure conditions of the Earth's surface is α-quartz.

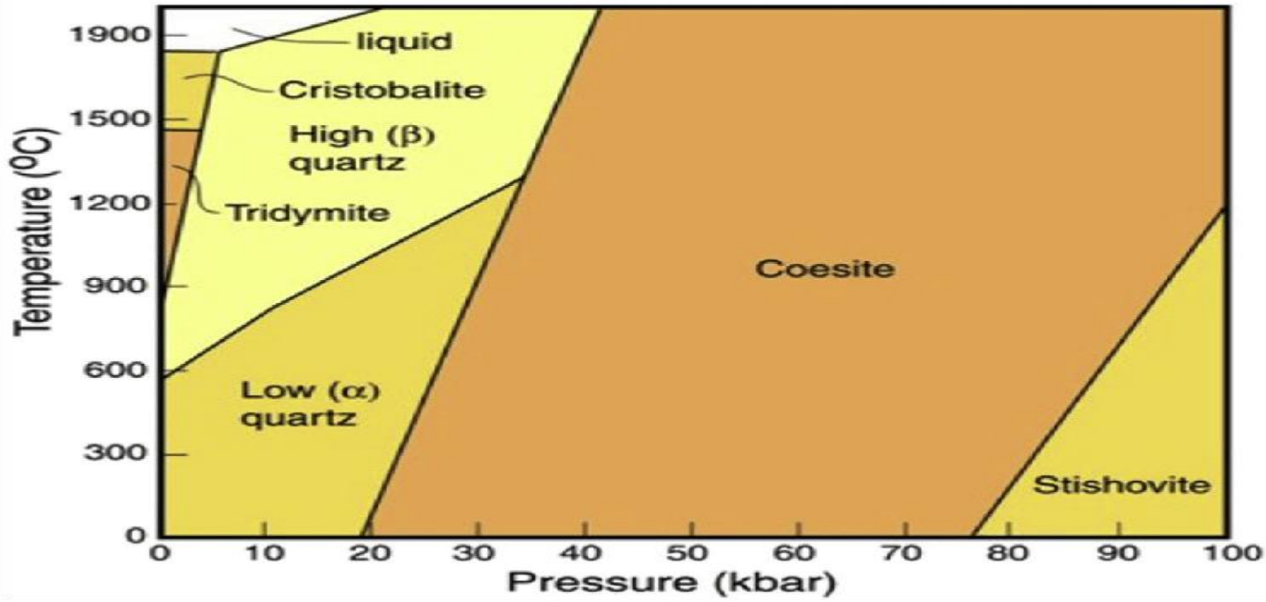

Figure 1: *Stability field of various forms of silica as a function of temperature and pressure. (According to Stephen A. Nilson)*

III.2.2. Feldspars:

Feldspars are the essential constituents of igneous, plutonic or effusive rocks (59.5% of the minerals in igneous rocks). Their **chemical composition** varies with the nature of the rocks: acidic rocks contain alkali feldspars, intermediate rocks contain alkali feldspars and medium plagioclases, basic rocks contain calcic plagioclases.

Feldspars belong to the tectosilicate family.

The analysis of feldspars allows them to be considered as more or less homogeneous mixtures of three elementary constituents:

- $KAlSi_3O_8$: Orthoclase (Gold) (Sanidine or microcline)
- $NaAlSi_3O_8$: Albite (Ab)
- $CaAl_2Si_2O_8$: Anorthite (An)

$KAlSi_3O_8$ and $NaAlSi_3O_8$ form a complete solid solution, called alkali feldspars; similarly, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ form a complete solid solution, called plagioclases. The composition of feldspars is usually represented in a triangular diagram:

- $KAlSi_3O_8$ [Orthoclase (Or)]
- $NaAlSi_3O_8$ [Albite (Ab)]
- $CaAl_2Si_2O_8$ [Anorthite (An)]

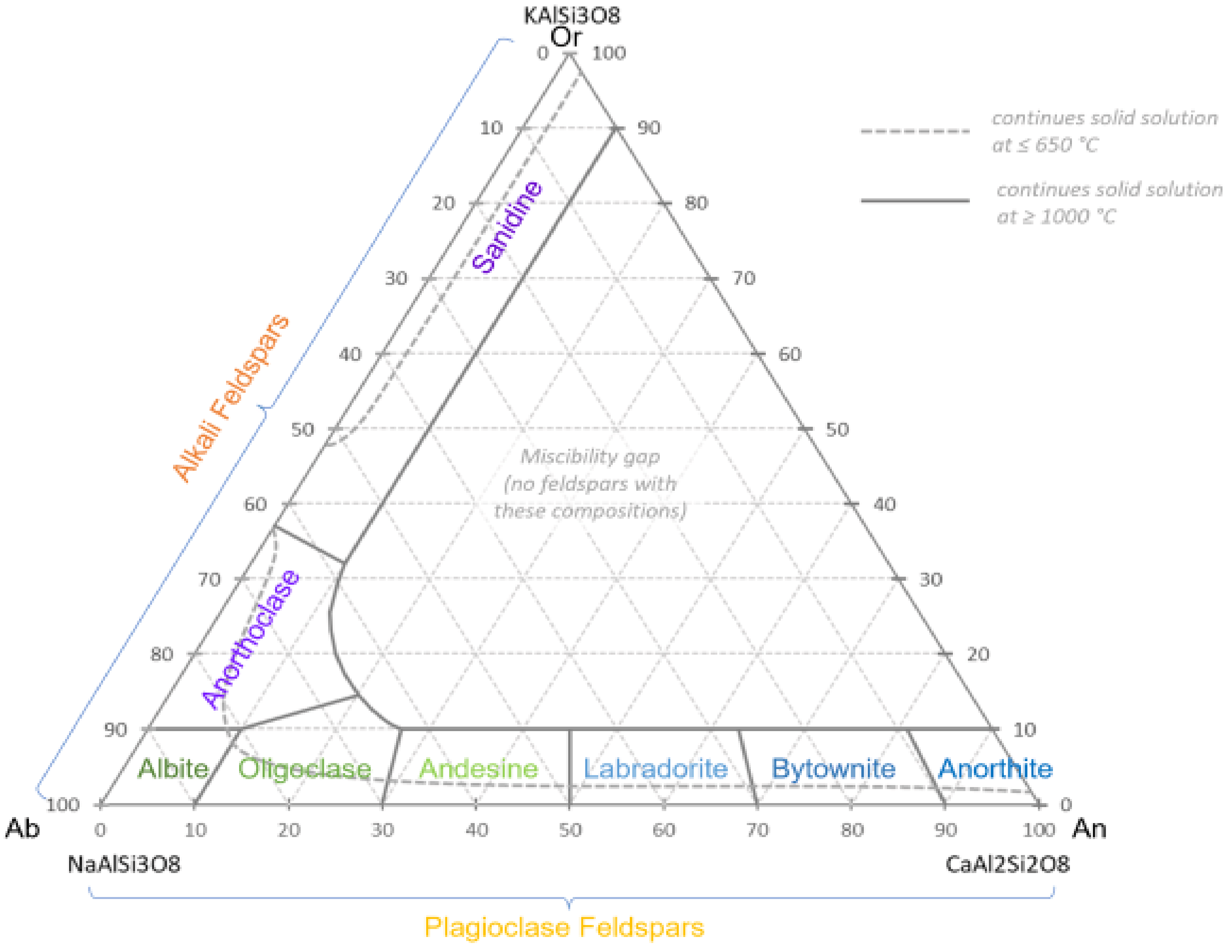

Figure 2: *The Feldspar Compositional Ternary Diagram. Christian Scheibe*

Alkali feldspars include two major types:

- **Potassium feldspars** (K,Na)$AlSi_3O_8$ with a low proportion of Na, corresponding to the microcline-orthoclase-sanidine series, with an increasingly disordered arrangement of Si and Al ions in the lattice. Orthoclase is the low-temperature potassium feldspar characteristic of granites. It crystallizes in the monoclinic system. Microcline is the ordered form of potassium feldspar stable at low temperatures. It is a secondary mineral, crystallizing in the triclinic system. Sanidine is the variety of high-temperature potassium feldspar, which has the most disordered structure.

- **Sodium-potassium feldspars** (Na,K)$AlSi_3O_8$, richer in Na than the previous ones, are intermediate between orthoclase and albite. Anorthoclase is on average made up of 60% orthoclase and 40% albite. It is a high-temperature mineral frequently associated with sanidine.

Plagioclase feldspars (triclinic feldspars) form a complete solid solution between the sodic albite pole (ab) and the calcic anorthite pole (an), and may contain a small amount of orthoclase (figure 2).

The different species distinguished are the following (An = anorthite = calcium content) (see also figure.02):

Albite (Ab100-90)

Oligoclase (Ab90-70)

Andesite (Ab70-50)

Labradorite (Ab50-30)

Bytownite (Ab30-10)

Anorthite (Ab10-0)

III.2.4. Feldspathoids:

Feldspathoids are aluminosilicates of Na and K, belonging to the tectosilicate family, very poor in silica, and which are found in rocks rich in Na_2O and K_2O (alkaline) and poor in SiO_2 (undersaturated). These minerals are incompatible with quartz, and except in rare exceptions, they cannot coexist with the latter in rocks. Feldspathoids have a composition similar to that of feldspars, but have a lower silica content.

The main feldspathoids are:

- **Nepheline** $Na_3K[AlSiO_4]$: hexagonal, essentially sodic, and transforms into albite in the presence of quartz.
- **Sodalite** $Na_8Al_6Si_6O_{24}Cl_2$: cubic, rare mineral accompanying nepheline.
- **Leucite** $KAlSi_2O_6$: quadratic at low temperature, and cubic at high temperature, rich in potassium, and transforms into orthoclase in the presence of quartz.

III.2.3. Olivines:

Olivines are found in **basic and ultra-basic rocks (mafic and ultra-mafic rocks).** They belong to the **Nesosilicate** family and form a complete solid solution ranging from the **magnesium pole**, ***Forsterite*** Mg_2SiO_4, to the **iron pole**, ***Fayalite*** Fe_2SiO_4.

The intermediates correspond to ***Olivine*** $(Fe, Mg)_2\ SiO_4$. Olivine forms at high temperatures, in quartz-free rocks, poor in SiO_2. Magnesian olivines are the most common, while iron-bearing olivines, or fayalites, are very rare. The latter are compatible with the presence of quartz and are found in acidic rocks (granites, rhyolites, etc.).

III.2.5. Pyroxenes:

Pyroxenes are mostly anhydrous silicates of calcium, magnesium or iron, which in some cases contain sodium, lithium and more rarely chromium and titanium. They crystallize in orthorhombic systems (orthopyroxenes) and monoclinic systems (clinopyroxenes).

The **classification of pyroxenes** is based largely on their respective **Ca, Mg, Fe** contents (chemical composition) and on their crystallographic systems, and appears on a triangular Ca-Mg-Fe diagram (figure 3). We thus distinguish:

- **Orthopyroxenes**, practically devoid of calcium, form a continuous series between a magnesium pole, the **Enstatite** $Mg_2Si_2O_6$, and a ferrous pole, the **Ferrosilite** $Fe_2Si_2O_6$. The **intermediates** constitute the **Hypersthenes** $(Mg,Fe)_2Si_2O_6$.
- **The clinopyroxenes**, calcic, monoclinic, include, on the one hand, the series that goes from Diopside $CaMgSi_2O_6$ to Hedenbergite $CaFeSi_2O_6$, on the other hand the large group of Augites, (*Augite is closely related to the* Diopside-Hedenbergite *series with addition of Al* and *minor Na substitution - $(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$)*, and finally the Pigeonites, very poor in calcium (*Ca substituting for Fe, and Mg*).
- **The pyroxenes** rich in sodium Na and lithium Li form the alkaline clinopyroxenes (rare minerals), of the monoclinic system with Spodumene $LiAlSi_2O_6$, Jadeite NaAl Si_2O_6 and Aegirine Fe_3+$NaSi_2O_6$.

The compositional range of the Ca-rich, Al-free pyroxenes in shown in the triangular composition diagram here. Note that there is complete Mg-Fe substitution and small amounts of Ca substitution into the Orthopyroxene solid solution series. ***Mg-rich varieties of orthopyroxene*** *are called* ***hypersthene****, whereas* ***Fe-rich varieties*** *are called* ***Ferrosilite****. There is also complete Mg-Fe solid solution between Diopside and Ferrohedenbergite, with some depletion in Ca. $CaSiO_3$ is the chemical formula for wollastonite, but wollastonite does not have a pyroxene structure.*

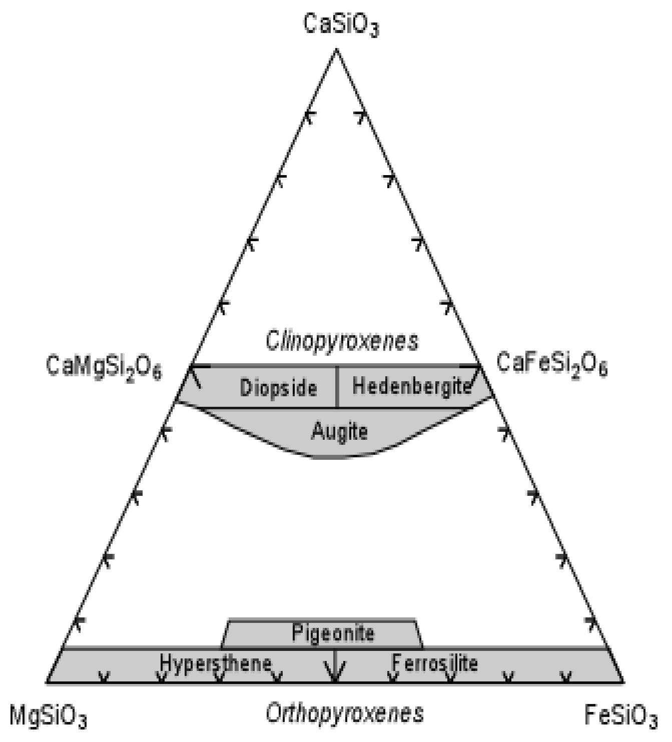

Figure 3: *Representation of pyroxenes in triangular diagram Ca-Mg-Fe*

(According to Stephen A. Nilson)

III.2.6. Amphiboles:

Amphiboles are **ferromagnesian silicates**. They are mainly found in **plutonic and metamorphic rocks**. They belong to the inosilicate family.

Amphiboles are mostly hydroxylated silicates (OH^- ion) of iron and magnesium, which contain large quantities of calcium, aluminum, sodium, lithium or titanium. They generally crystallize in the monoclinic system.

The classification of amphiboles is complex and largely linked to the progressive variations in the Mg, Fe, Ca, and Na contents. We thus distinguish (Figure 4):

- **Ferromagnesian amphiboles**: of the formula $(Mg,Fe)_7[Si_8O_{22}](OH)_2$, which only exist in metamorphic rocks.
- **Calcium amphiboles**: which may or may not be aluminous.
    - **Non-aluminous calcium amphiboles** form a continuous series between a magnesium pole, **Tremolite** $Ca_2Mg_5Si_8O_{22}(OH)_2$ and a ferrous pole, **Ferroactinolite** $Ca_2Fe_5Si_8O_{22}(OH)_2$, the **Actinolites** constitute the intermediate terms $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$. They only exist in metamorphic rocks.

    - **Aluminous calcium amphiboles** form the vast group of hornblendes, with the formula $(Ca,Na,K)_2(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH,F)_2$. These are the most common amphiboles and are found in calc-alkaline plutonic rocks and in metamorphic rocks. We should also mention the existence of basaltic hornblende, which is much less common.

- **Sodium amphiboles:** form a continuous series between **Glaucophane** $Na_2Mg_3Al_2Si_8O_{22}(OH)_2$ and **Riebeckite** $Na_2Fe_2^{+3}Fe_3^{+}2\ Si_8O_{22}(OH)_2$. Glaucophane is limited to metamorphic rocks, while riebeckite appears mainly in alkaline plutonic rocks.

*Numerous common amphiboles can be represented within the $Mg_7Si_8O_{22}(OH)_2$ (anthophyllite), $Fe_7Si_8O_{22}(OH)_2$ (grunerite) and $Ca_7Si_8O_{22}(OH)_2$ (hypothetical pure calcium amphibole). This diagram is commonly referred to as the **amphibole quadrilateral**.*

Complete substitution extends from tremolite [$Ca_2Mg_5Si_8O_{22}(OH)_2$] to ferro-actinolite [$Ca_2Fe_5Si_8O_{22}(OH)_2$]. Actinolite is the intermediate member of the tremolite-ferro-actinolite series. The compositional range from $Mg_7Si_8O_{22}(OH)_2$ to about $Fe_2Mg_5Si_8O_{22}(OH)_2$ is represented by the orthorhombic amphibole known as anthophyllite. The monoclinic cummingtonite-grunerite series exists from about $Fe_2Mg_2Si_8O_{22}(OH)_2$ to $Fe_7Si_8O_{22}(OH)_2$. Intermediate amphibole compositions do not exist between anthophyllite and the tremolite-actinolite series

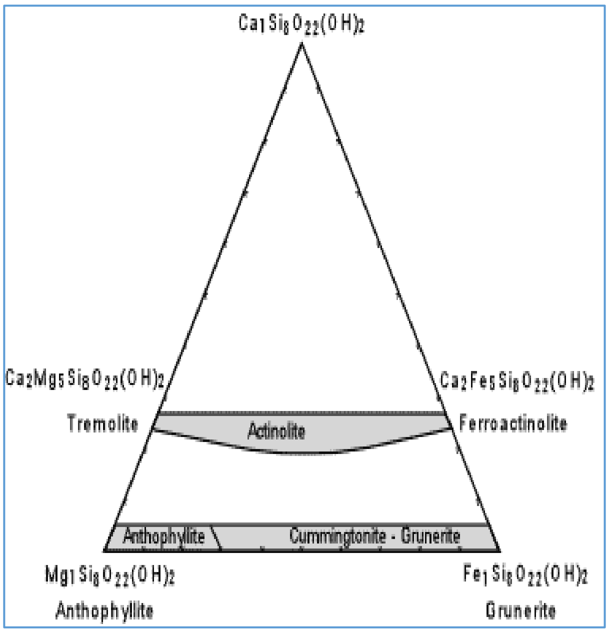

Figure 4: *Representation of Amphiboles in triangular diagram Ca-Mg-Fe*

(According to Stephen A. Nilson)

III.2.7. Micas:

Micas are hydrated silicates, more or less aluminous and almost always potassic, which contain iron and magnesium in variable proportions. They belong to the phyllosilicate family and are monoclinic. We distinguish:

- **White aluminous micas**: mainly with Muscovite $KAl_3Si_3O_{10}(OH)_2$, and its sodium equivalent, **Paragonite** $NaAl_3Si_3O_{10}(OH)_2$. These minerals are common in acidic plutonic rocks.
- **Ferromagnesian black micas**: represented mainly by **Biotites**, which are intermediate minerals between a magnesium pole, Phlogopite $KMg_3AlSi_3O_{10}(OH)_2$ and an iron pole, **Annite** $KFe_3AlSi_3O_{10}(OH)_2$.
  Biotites are very common in igneous rocks (especially acidic and intermediate).
- **Lithium micas**, represented by **Lepidolite** $K(Li, Al)_2AlSi_3O_{10}(OH)_2$, are present in pegmatites.

III.2.8. Accessory Minerals: accessory minerals include **Iron** and **titanium oxides**:

- **Magnetite** Fe_3O_4: cubic system. The most common accessory mineral
- **Hematite** Fe_2O_3: hexagonal system. It frequently represents the alteration product of magnetite or forms a solid solution with ilmenite in unaltered igneous rocks.
- **Ilmenite** $FeTiO_3$: hexagonal system. Main ore of titanium. Common in
  - a wide variety of volcanic and plutonic rocks.
- **Spinel** $MgAl_2O_4$: cubic system. Common in ultrabasic rocks and sometimes in basalts.
- **Corundum** Al_2O_3: hexagonal system. It is common in igneous rocks rich in aluminum (Al).
- **Apatite** $Ca_5(PO_4)_3(OH,F)$: hexagonal system. Very common in alkaline magmatic rocks (granites, syenites, pegmatites and equivalent lavas).
- **Zircon** $ZrSiO_4$: quadratic system. It is common in siliceous magmatic rocks (granites, granodiorites, syenites). It often contains traces of radioactive elements (Th and U). This mineral is thus used to date rocks with the U-Pb and Th-Pb method.
- **Sphene** $CaTiSiO_4(OH)$: monoclinic system. It is widespread in many magmatic rocks (granites, granodiorites, syenites).
- **Pyrite** FeS_2: cubic system. It is widespread in various magmatic rocks.
- **Calcite** $CaCO_3$: rhombohedral system. It is present in carbonatites.
- **Fluorine** (or fluorite) CaF_2: cubic system (fluorine ore). It is present in alkaline igneous rocks (granites, syenites, pegmatites).

III.3. The order of appearance of minerals in igneous rocks:

The order of appearance of minerals in igneous rocks is mainly determined by the Bowen reaction series theory, which describes the evolution of minerals during the cooling of a magma. High-temperature minerals crystallize before low-temperature minerals. Here are some important points regarding the order of appearance of minerals in igneous rocks:

- The first phases of crystallization include **olivine**, then **pyroxenes** and **amphiboles**.
- **Biotite** (black mica), **calcium-rich plagioclases**, **orthoclase**, **muscovite** (white mica) and finally **quartz**.

The order of appearance of minerals can vary slightly depending on the initial chemical composition of the magma, the presence of water, and the pressure at which crystallization occurs2

In summary, the order of appearance of minerals in igneous rocks is determined by the Bowen reaction series, which takes into account the temperature and chemical composition of the magma.

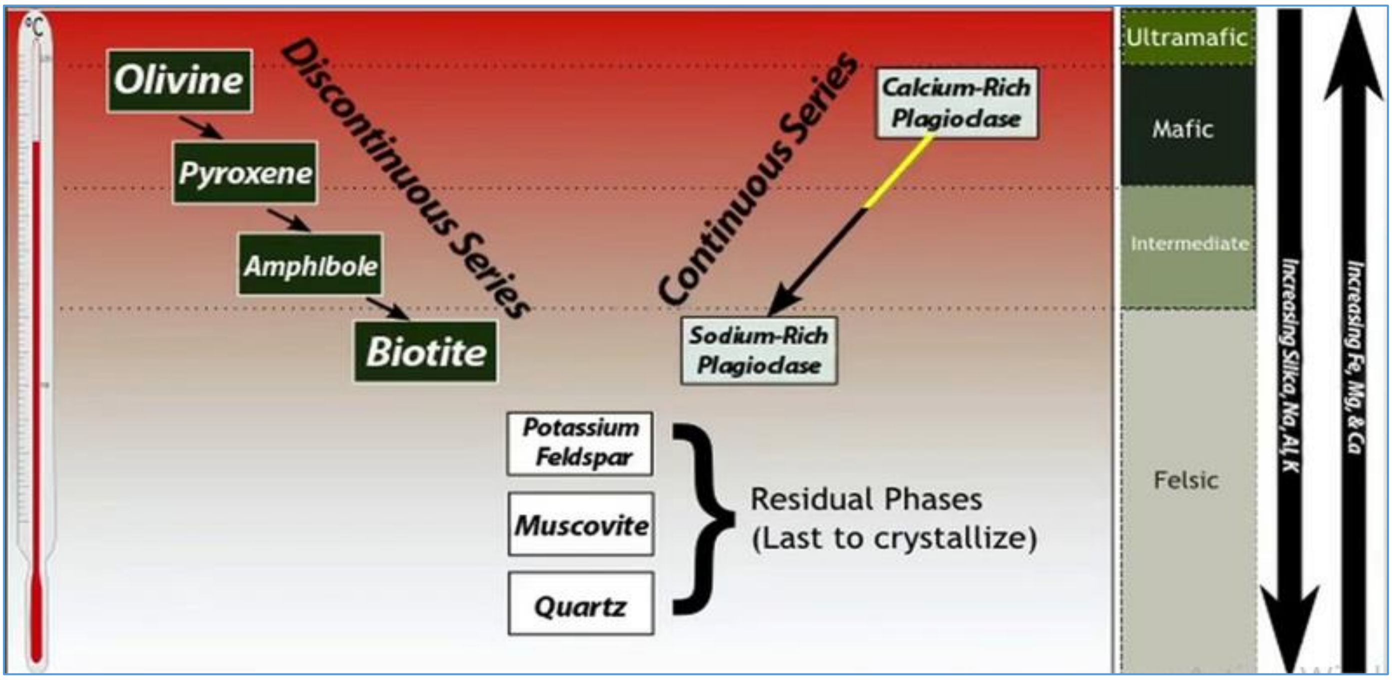

Figure 5: *Bowen's Reaction Series. Minerals that crystallize at higher temperatures are at the top (olivine) and minerals that crystallize at lower temperatures are at the bottom (quartz). (Source Colivine, modified from Bowen, 1922)*

Minéral	Formule chimique	Roches magmatiques
Silice		
Quartz, tridymite, cristobalite	SiO_2	Roches acides
Feldspaths		
Sanidine, orthose, microcline	$KAlSi_3O_8$	Volcaniques (sanidine) et plutoniques
Plagioclases		
Albite	$NaAlSi_3O_8$	Roches volcaniques et plutoniques,
Anorthite	$CaAlSi_3O_8$	acides et basiques.
Feldspathoïdes		
Népheline	$Na_3K[AlSiO_4]$	Roches alcalines pauvres en SiO_2
Leucite	$KAlSi_2O_6$	
Sodalite	$Na_8Al_6Si_6O_{24}Cl_2$	
Olivines		
Fayalite	Fe_2SiO_4	Roches acides
Forstérite	Mg_2SiO_4	Roches basiques et ultrabasiques
Pyroxènes		
Enstatite	$Mg_2Si_2O_6$	Roches volcaniques et plutoniques
Hypersthène	$(Mg,Fe)_2Si_2O_6$	// // //
Augite	$Ca(Mg,Fe)Si_2O_6$	// // //
Aegyrine	$Fe^{3+}NaSi_2O_6$	Roches alcalines – granite et syénite
Spodumène	$LiAlSi_2O_6$	
Amphiboles		
Hornblende	$(Ca,Na,K)_{2-3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH,F)_2$	Roches plutoniques calcoalcalines
Riébeckite	$Na_2Fe^{3+}_2Fe^{2+}_3Si_8O_{22}(OH)_2$	Roches plutoniques alcalines
Micas		
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Roches plutoniques acides
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Roches magmatiques acides et inter.
Lépidolite	$KLi_2Al(Si_4O_{10})(OH)_2$	Pegmatites
Minéraux accessoires		
Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	Roches magmatiques alcalines
Corindon	Al_2O_3	Roches magmatiques riches en Al
Sphène	$CaTiSiO_5$	Roches magmatiques alcalines
Fluorine	CaF_2	Roches magmatiques alcalines
Zircon	$ZrSiO_4$	Roches magmatiques siliceuses
Magnétite	$FeFe_2O_4$	Grande variété de roches
Ilménite	$FeTiO_3$	magmatiques
Pyrite	FeS_2	

Tableau 1 : Principaux minéraux des roches magmatiques.