

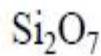
II-2 SILICATES

II-2-1 General

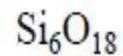
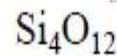
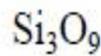
Silicates are the main constituents of eruptive and metamorphic rocks. They alone constitute 80% of the earth's crust. If we still add quartz, we must increase this figure to 92%.

The anionic group [**SiO₄**] consists of a small silicon atom surrounded by four large oxygen atoms which occupy the vertices of an imaginary tetrahedron. It is usually called the SiO₄ tetrahedron. This group is very difficult to separate. In addition, it has the particularity of being able to form polymers by sharing certain oxygen atoms. In other words, they can combine either in groups of 2 tetrahedra, or in rings of 3, 4 or 6 tetrahedra, or even in chains of indefinite length, in layers and even in three-dimensional frames.

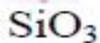
The classification is therefore based on the degree of polymerization of the tetrahedra.



Two tetrahedra



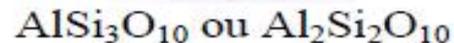
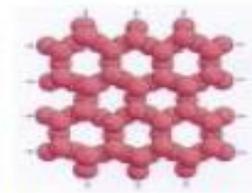
Rings of three, four or six tetrahedral



Single chain



Double chain Layer



polymerized tetrahedra

Polymerization of SiO ₄ tetrahedra	
nesosilicates:	tetrahedra isolated from each other
others.	
sorosilicates:	groups of 2 tetrahedra.
cyclosilicates:	rings of 3, 4 or 6 tetrahedra.
inosilicates:	chain polymerization.
Phyllosilicates	three-dimensional framework

In highly polymerized silicates (chains, layers, frameworks), the Silicon atoms are often partially replaced by aluminum. We then encounter a certain proportion of $[\text{AlO}_4]$ tetrahedra among the tetrahedral $[\text{SiO}_4]$. We then speak of aluminosilicates.

The main chemical elements that make up the chemical composition of silicates are: O, Si, Al, Fe, Mn, Mg, Ca, K, as well as Li, Be, B, Ti, En and H under form of (OH) or H_2O .

II-2-2 Structural classification of silicates

Until 1920, silicate chemistry was limited to the knowledge of the crude formula, formula which did not make it possible to predict the properties of a mineral.

X-ray diffraction for the establishment of structural formulas had to be fundamental (works by Bragg, Pauling, Mauguin, etc.).

Currently no one can ignore the classification of silicates. This makes it possible to establish correlations between the structure and properties of minerals.

Silicon and oxygen being the most abundant chemical elements in the earth's crust (they together account for $\frac{3}{4}$ of all materials), it is therefore not surprising that a group of minerals, composed of 2 of these elements (Si and O) plus a certain number of ions, called silicates, make up 95% of the volume of the earth's crust.

All silicates have a basic structure composed of Si^{4+} and O^{2-} ions. The Si^{4+} ions being housed in the center of a tetrahedron whose vertices are occupied by O^{2-} . This is the $[\text{SiO}_4]^{4-}$ tetrahedron. The O^{2-} anions are grouped around silicon in the form of regular tetrahedra $[\text{SiO}_4]^{4-}$ because $R_i(\text{Si}^{4+}) / R_i(\text{O}^{2-}) = 0.30$ which implies that the coordination of Si is IV.

Silicates can be classified according to the different modes of linking the $[\text{SiO}_4]^{4-}$ tetrahedra. We will first return to the coordination of ions before tackling the arrangement of polyhedra and their sequence.

II-2-2-1 Coordination

Since oxygen ions form compact stacks in the structure of silicates, we will therefore define the coordination with respect to oxygen.

Thus the Si^{4+} ion, given its ionic radius, admits a coordination of IV (tetrahedral), the Al^{3+} ion, a coordination of IV or VI, as for the ions Mg^{2+} , Fe^{2+} , Fe^{3+} , Ti^{4+} with fairly similar ionic radii, they admit an entourage of 6 oxygens. The alkalis K and Na have coordinations greater than VI.

II-2-2-2 Arrangement of polyhedra

In the “silicate framework” where the $[\text{SiO}_4]^{4-}$ tetrahedra only have the vertices in common, Al can be either within the tetrahedra in substitution for Si (case of aluminosilicates), or at the center of AlO_6 octahedrons (alumina silicates).

On the other hand Mg, Fe, Ti, Na, Ca, K are at the center of octahedra (XO_6) which will have vertices and edges in common for (AlO_6 , FeO_6 , MgO_6 , TiO_6), or even faces in common for (NaO_6 , CaO_6 , KO_6). These characteristics, the pooling of a certain number of vertices, edges or faces, are imposed by Pauling's rules.

The main cations which will form the framework of the groups in order to ensure the cohesion and electro-neutrality of the crystalline structure are:

Li^+ , Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Al^{3+} , Cr^{3+} , Ti^{4+} , all of VI coordination

Na^+ , K^+ , R^{b+} , Cs^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} of coordination VIII.

II-2-2-3 Chaining of tetrahedra $[\text{SiO}_4]^{4-}$.

We define the structural classes of silicates on the basis of the sequence of vertices of $[\text{SiO}_4]^{4-}$ tetrahedra. The number of oxygens or vertices that the tetrahedron (SiO_4) shares with its neighbors reflects the state of polymerization of the silicate framework. This state gives the silicates their morphology, their facies, the physical properties (cleavage, birefringence and stability). We thus distinguish:

II-2-3 NESOSILICATES AND SUBNESOSILICATES

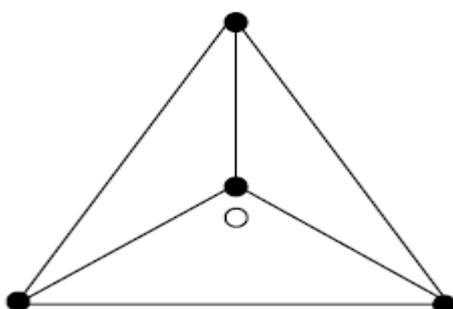
These silicates with isolated tetrahedra are classified into 2 subgroups:

- True neso-silicates
- Subneso-silicates which contain additional anionic polyhedra

II-2-3-1 NESOSILICATES (Silicates with isolated tetrahedra)

It is a monomeric silicate framework formed of independent tetrahedra. The $[\text{SiO}_4]^{4-}$ ions are linked together by cations (Fe, Mg, Ca etc...).

Neso-silicates Isolated ions (tetrahedra): $[\text{SiO}_4]^{4-}$ belong to crystal systems of high symmetry, have isometric morphologies, high refractive indices and slightly pronounced cleavage properties.



Nesosilicates

- Oxygène (4 O)
- Silice (1 Si)

True nesosilicates They are classified according to the size of the cations which connect the tetrahedra together in:

-Nesosilicates with small cations: **Phenacite** (SiO₄) Be₂

-Medium cation nesosilicates: **Olivine** (SiO₄) (FeMg)₂ **garnets** (SiO₄)₃(Al, Fe,Cr)₂(Ca,Fe,Mg,Mn)₃

-Nesosilicates with large cations: **Zircon** (SiO₄) Zr . Only neso-silicates with medium cations and subneso-silicates will be studied.

II-2-3-1-1 Group of peridot

Peridot is a ferromagnesian mineral forming a continuous solid solution between a Mg pole which is **Forsterite** of formula (SiO₄) Mg₂ and an Fe pole which is **Fayalite** of formula (SiO₄) Fe₂ the intermediate term being olivine: (SiO₄) (FeMg)₂, mineral well known in petrography.

Olivine crystallizes in the orthorhombic system (mmm).

It is rarely automorphic and often appears as a nodular grainy mass. It is yellow green to olive green in color, with a hardness between 6.5 and 7 and a density between 3.25 and 4.

Au microscope l'olivine présente une réfringence et une biréfringence moyenne à forte, cette dernière croît avec la teneur en fer.

Gisement : l'olivine est un minéral fréquent dans les roches magmatiques basiques (basaltes et gabbros) et ultrabasiques péridotites (dunites).

La forstérite, rare dans les roches magmatiques est plutôt un minéral des roches métamorphiques qui apparaît lorsque des sédiments placés dans des conditions de pression et de température élevées se transforment en calcaire cristallin d'après la réaction suivante :



La fayalite est un péridot qui cristallise dans les milieux très différenciés enrichis à la fois en Fe et en Na. La fayalite se rencontre dans quelques phonolites, trachytes et leurs équivalents grenus.

Altération : les olivines sont souvent transformées soit en serpentine ou en iddingsite de couleur rougeâtre correspondant à un mélange d'oxydes de fer, Mg et de goethite (FeO,OH). Les agents d'altération sont soit des gaz tardimagmatiques soit des liquides.

Species	Colors	Hardness	Density
Almandin	Pink to red-brown	7	4.25
Pyrope	Garnet	7 to 7.5	3.51
Grossular	Colorless, pinkish to yellow-green	6.5	3.53
Spessartine	Yellow to red-brown	7 to 7.5	4.18
Andradite	Green to brown-black	7	3.75
Uvarovite	Emerald green	7	3.77

II-2-3-1-2 Garnet Group

They form complex solid solutions with the general formula: $(\text{SiO}_4)_3 \text{Y}^{3+} \text{X}^{2+}$

With $\text{Y}^{3+} = \text{Al}^{3+}$, and $\text{X}^{2+} = \text{Fe}^{2+}, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Mn}^{2+}$

The names of the different species are grouped in the following table:

	Al^{3+}	Fe^{3+}	Cr^{3+}
Fe^{2+}	Almandin		
Mg^{2+}	Pyrope		
Ca^{2+}	Grossular	Andradite	Uvarovite
Mn^{2+}	Spessartine	Calderite	Mn^{2+}

Aluminous garnets and andradite are the most common.

Garnets all crystallize in the cubic holohedral $m\bar{3}m$ system. They are frequently automorphic and present an isometric facies consisting of the rhombododecahedron shape (110)? They can also appear in rounded grains.

Their color, refractive indices, hardness and density vary with their composition.

All garnets have a vitreous luster, they are transparent to translucent.

Deposit: Garnets are common minerals in metamorphic rocks and some igneous rocks. Thus we find:

Almandine in gneisses and mica schists.

Pyrope in peridotites and kimberlites.

The grossular in the skarns.

Spessartine in granites and granite pegmatites.

Andradite in contact metamorphism rocks.

Ouvarovite in chromiferous serpentinites.

II-2-3-2 SUBNESOSILICATES

These are alumina silicates corresponding to the minerals of metamorphism, these are andalusite, sillimanite and kyanite.

These are polymorphic minerals responding to the overall composition: SiAl_2O_5

II-2-3-2-1 Andalusite

It crystallizes in the orthorhombic holohedron system mmm.

Very frequently automorphic: pseudoquadratic prismatic crystals elongated along Oz and combining the forms (110), (100), (010) and (001). Andalusite can also occur in radiated aggregates. It often contains carbonaceous inclusions at the limits of the sectors (110), this is the chialstolite variety.

Color: dirty white, gray to light brown. She has a very easy 010 cleavage.

It is translucent with a greasy shine. She presents an irregular break.

Hardness =7.5 and density: 3.1 to 3.2.

Deposit: andalusite is a mineral of contact metamorphism between granite and schists to give corneas. It is also a mineral of general or regional metamorphism, where it represents a mineral typical of moderate to low pressures (< 5 Kbars) and is then found in gneisses.

Andalusite weathers into muscovite and sericite.

II-2-3-2-2 Disthenes

It crystallizes in the triclinic holohedron system (1). They have 2 cleavages, an easy 100 cleavage and a more difficult 010 cleavage.

Kyanite is frequently automorphic and it then presents a prismatic facies elongated according to (001) and flattened according to (100). It often occurs in radiated aggregates.

Color: colorless to sky blue or brownish.

Kyanite is transparent to translucent and has an oily sheen on cleavages.

Hardness: 4 to 7, density: 3.5 to 3.7 it is the densest variety of alumina silicates.

Deposit: kyanite is a mineral found almost exclusively in gneisses

and mica schists where it coexists with garnet.

Kyanite alters to muscovite.

II-2-3-2-3 Sillimanite

It crystallizes in the orthorhombic holohedron system mmm, and presents very easy 010 cleavages.

Sillimanite is rarely automorphic, it presents an acicular to fibrous facies elongated along Oz with the shapes (010) and (110) sometimes visible. It can also appear in flexuous capillary aggregates.

Color: whitish to light brown.

It is transparent to translucent with a greasy shine and a flaky break.

Hardness 6 to 7, density=3.3.

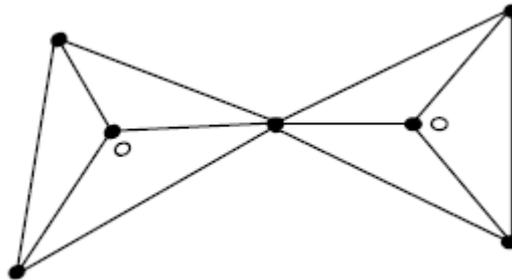
Deposit: Sillimanite is a mineral of general catazone metamorphism (high temperature above 550°C and high pressure). It is present in Sillimanite gneisses. No known alteration.

N. B. The three (03) polymorphs: Andalusite, Kyanite and Sillimanite only exist in rocks where aluminum is in excess compared to most of the other elements.

The least dense Andalusite forms by metamorphism under low pressure and Kyanite which is the densest and forms under high pressure.

II-2-4 SORO-SILICATES (Silicates with tetrahedra associated in pairs)

Sorosilicates contain $[\text{Si}_2\text{O}_7]^{6-}$ groups formed by two tetrahedra linked together. The framework is dimeric. True soro-silicates are rare, while complex sorosilicates containing both $[\text{SiO}_4]$ and $[\text{Si}_2\text{O}_7]$ are more common. Soro-silicates have the same properties as nesosilicates. Ions coming from the meeting of two SiO_4 tetrahedra: $[\text{SiO}_2\text{O}_7]^{6-}$.



Soro-silicates have in common the dimer combination of silicate tetrahedra: $[\text{Si}_2\text{O}_7]^{6-}$, sorosilicates are classified into three (03) groups:

Sorosilicates are isolated silicates (Si_2O_7). We distinguish:

1. True soro-silicates: Melilite group
2. Subsoro-silicates: group of epidotes and Idocrase
3. Subsorosilicates with additional oxygen ions: Lawsonite group

Only **subsorosilicates** with the epidote group will be the subject of our study.

II-2-4-1 Epidotes

Minerals in this group exhibit both (Si_2O_7) and (SiO_4) functions as well as additional oxygen ions not bonded to silicon. We distinguish:

II-2-4-2 Zoisite (Si_2O_7) (SiO_4) O (OH) Al_3Ca_2

It comes in 2 forms: orthorhombic and monoclinic (clino-zoisite)

II-2-4-3 Pistachite (Si_2O_7) (SiO_4) (OH) $\text{Ca}_2\text{FeAl}_2\text{O}$

It is an epidote which contains 10% of Fe_2O_3 molecules, it crystallizes in the monoclinic system.

II-2-4-4 Piemontite (Si_2O_7) (SiO_4) O (OH) $(\text{Al}, \text{Fe}^{3+}, \text{Fe}^{2+}, \text{Mn}^{2+})_3(\text{Ca}, \text{Ce}, \text{La}, \text{Y}^{3+})_2$

It is a variety that contains manganese and crystallizes in the monoclinic system.

II-2-4-5 Allanite or orthotis



In general, epidotes appear in the form of prismatic crystals that can reach around thirty cm, sometimes acicular, with frequent flattening. They can appear in fibro-radiated groups or in grainy masses.

Color: bottle green to pistachio green tending towards yellow or black. Piedmontite is purplish brown in color

Irregular breakage, sometimes lamellar. Cleavage parallel to elongation.

Translucent to opaque, with a vitreous sheen.

Hardness between 6 and 7, and density = 3.4

Deposit: epidotes are found in rocks of low regional metamorphism. Allanite is found in acidic eruptive rocks: granites, granodiorites and pegmatites.

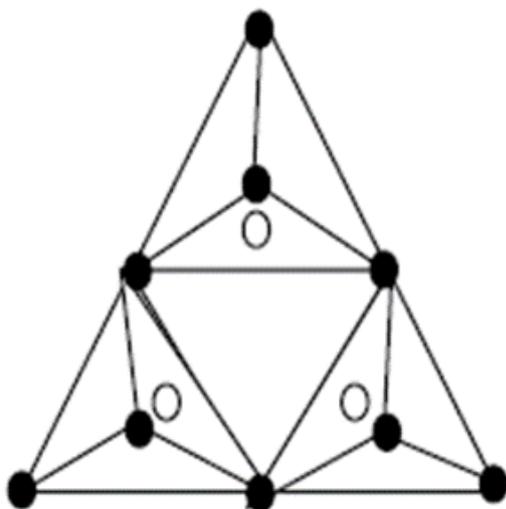
Product of hydrothermal alteration of alumino-calcium silicates (feldspar, hornblende)

-2-5 CYCLOSILICATES (Silicates with tetrahedrons associated in rings)

The rings have 3, 4 or 6 tetrahedra, hence the structural formulas:

$[\text{Si}_3\text{O}_9]^{6-}$, $[\text{Si}_4\text{O}_{12}]^{8-}$, $[\text{Si}_6\text{O}_{18}]^{12-}$, the rings of tetrahedrons constitute the framework of cyclo-silicates. The corresponding species belong to the system: rhombohedral, quadratic, hexagonal.

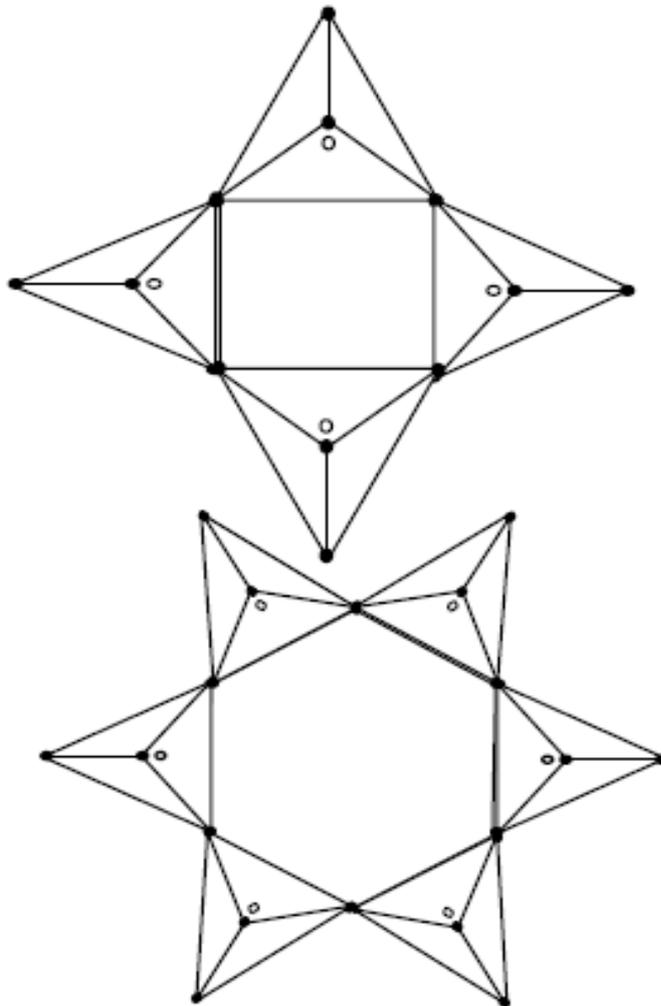
Anions made up of tetrahedra so as to form rings - these can comprise three (03) $[\text{Si}_3\text{O}_9]^{6-}$, four $[\text{Si}_4\text{O}_{12}]^{8-}$ or six $[\text{Si}_6\text{O}_{18}]^{12-}$ tetrahedra - these are cyclo-silicates.



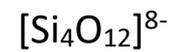
Cyclo-silicates

A- Rhombohedral system $[\text{Si}_3\text{O}_9]^{6-}$

- Oxygen (9 O)
- Silica (3 Si)

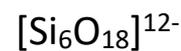


B- Quadratic system



- Oxygen (12 O)
- Silica (4 Si)

C- Hexagonal system



- Oxygen (18 O)
- Silica (6 Si)

Cyclo-silicates, as we said in the introduction, cyclosilicates are distinguished by particular features, namely that the crystal lattices contain isolated groups of SiO_4 tetrahedra associated in rings, that is to say characterized by complex radicals:

(Si_4O_{12}) and (Si_6O_{18}).

We distinguish 2 groups:

A group of 4 tetrahedra associated in rings: axinite

A group of 6 tetrahedra associated in rings: beryl, tourmaline and cordierite.

The minerals of the 2nd group are the most important.

II-2-5-1 The Beryl group

It is the most widespread mineral containing beryllium.

Beryl with the formula (Si_6O_{18}) $\text{Be}_3 \text{Al}_2$ crystallizes in the hexagonal system.

Beryl has a prismatic appearance. It is generally found in the form of isolated crystals, sometimes grouped in druses.

Color: varied: often greenish white, yellow green, light blue, bright green, sometimes pink.

Depending on the color we distinguish:

- emerald: bright green beryl. Translucent varieties without cracks are highly sought after gems (coloring due to Cr^{3+}).

- Aquamarine: variety of transparent blue beryl.

Density: between 2.6 and 2.9.

Hardness: between 7.5 and 8.

Deposit: common mineral of pegmatites, granites and nepheline syenites.

Beryl can arise by metasomatism in a metamorphic context (e.g. Siberian emeralds) or sedimentary context (e.g. Colombian emeralds).

Large deposit in Brazil, India and South Africa.

Beryl is used in the aeronautical industry because Be is one of the lightest metals. It is also used medicinally as Be salts.

II-2-5-2 The Tourmaline group

Its formula is as follows: $[(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH}, \text{F})_4]\text{Al}_6\text{Y}_3\text{Na}$.

In which **Y = Mg, Fe, Mn, Li, Al**

When **Y = Mg**, tourmaline is called magnesium, it is yellow-brown dravite.

When **Y = (Fe, Mn)** tourmaline is said to be ferrous, it is black schörl. When **Y = (Al, Li)**, it is an alkaline tourmaline, pink or blue colored Elbaite. The color of Tourmaline therefore depends on its chemical composition.

Tourmaline crystallizes in the rhombohedral system, it is in the form of long striated crystals following the elongation (columnar facies) with a triangular section, often curved. It can appear in acicular or fibrous aggregates.

Conchoidal breakage, no cleavage

Transparent to opaque, and glassy sheen

Density between 2.9 and 3.2. Hardness = 7 to 7.5

Deposit: Tourmaline is a mineral typical of pneumatolitic environments. We meet her:

- In Pegmatites where it coexisted with quartz and Orthoclase and with Muscovite.
- In Granites and Greisens with Cassiterite, topaz and Wolframite.
- In high temperature Gold deposits.
- In crystalline shales.

II-2-5-3 The Cordierite group

Of formula: $(\text{Si}_5\text{AlO}_{18})(\text{Mg, Fe})_2\text{Al}_3$ it crystallizes in the orthorhombic system, with a crystal structure comparable to that of beryl with aluminum ions in place of Be.

The crystals are rare, it appears in grains or in compact masses

Color: it can be colorless but often colored: gray, blue, blue-violet, rarely yellowish white or brown.

Its luster is glassy, transparent to translucent.

Irregular to conchoidal breakage. Next sharp cleavage 010

Hardness between 7 and 7.5

Density between 2.60 and 2.66

Cordierite weathers into pinitite

Deposit: Cordierite is common in rocks of general metamorphism (Gneisses, Granulites, Migmatites) in rocks of contact metamorphism (Schists and Corneals) but also in igneous rocks (Pegmatites and anatexia granites).

II-2-6 INO-SILICATES (Silicates with chain tetrahedrons.....Next