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Ministry of Higher Education and Scientific Research
8 May 45 University, Guelma

Faculty of Natural and Life Sciences and Earth and Universe Sciences

Department of Natural and Life Sciences

كلية علوم الطبيعة و الحياة و علوم الارض و الكون

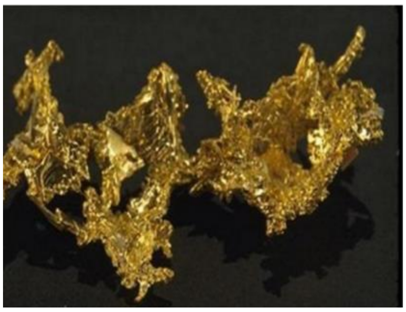
قسم علوم الطبيعة و الحياة

Course handout

MINERALOGY

Destined for the Second year Geology (L2) Bachelor's degree

Presented by: *Dr. Boulemia Salim*



Academic Year: 2024/2025

FUNDAMENTAL TEACHING UNIT I (**UEF 312**)

(Credits: 6; Coefficients: 3)

Subject 1: **Mineralogy**, Semester: 3

Course : 01H30 TP : 03h00

TEACHING OBJECTIVE:

The teaching of mineralogy aims to acquiring skills in order to define, recognize and classify minerals, that is to say natural products which do not come from plants or animals, distinguished from each other by their chemical compositions and their physical properties (color, luster, hardness, etc.).

COURSE STRUCTURE AND CONTENT

Chapitre I : Notions de Cristallochimie

1. Rappels de quelques définitions (cristal, minéral etc …)
2. Rappels de la structure de l'atome et des liaisons chimiques
3. Définition de la coordinance, isotypisme, isomorphisme et polymorphisme.

Chapitre II : Classification des minéraux

1- Classe des silicates
2- éléments natifs.
3- Classe des halogénures.
4- Classe des sulfures et sulfosels.
5- Classe des oxydes et hydroxydes.
6- Classes des carbonates…
7- Classes des sulfates…
8- Classe des phosphates…
9- Classe des borates

Summary

CHAPTER I: Notions of Crystallo-chemistry

3. Definition Of Coordination, Isotypism, Isomorphism and Polymorphism

Chapter II : Mineral's Classification

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Chapter I

Notions of Crystallo-chemistry

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1. Reminders of some definitions (crystal, mineral, etc.)

Modern **mineralogy** dates since the 18th century, literally meaning the study of minerals. It is a discipline (specialty) of earth sciences which studies the constituents (minerals) of rocks and ores in the terrestrial globe. These minerals, numbering around 4000 species, are distinguished from each other by their chemical compositions and their physical properties (color, luster, hardness, etc.). Otherwise, mineralogy aims to define, recognize and classify minerals, that is to say natural products which do not come from plants or animals.

A mineral is a natural, homogeneous solid substance (with the exception of mercury), having a well-defined chemical composition and possessing a set of characteristic properties (color, cleavage, luminescence, etc.). It often has an ordered atomic structure (with the exception of amorphous minerals). The minerals used to obtain a metal after metallurgical treatment are called **ores**.

A crystal; is often identified by a geometric shape and the presence of repeating flat surfaces (faces) and angles. This geometry reflects what we call the crystalline state. A crystal is a body characterized by the ordered arrangement of its constituent atoms. However, crystals do not always have geometric shapes, simply because they did not have sufficient space to acquire them; we speak of xenomorphic crystals, as opposed to automorphic.

Crystals and Polyhedron shapes: The formation of crystals from simple ions follows simple empirical rules called Pauling's rules. Around each cation are arranged anions, which occupy the vertices of a polyhedron. The nature of the polyhedron (called coordination polyhedron) is; defined by the ratio of the radius of the cation to the radius of the anion (Rc/Ra). The shapes are as compact as possible. The connections between polyhedra are less stable when they are made via edges or sides; polyhedra are therefore generally associated by

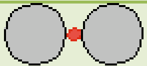
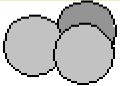
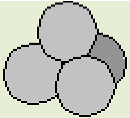
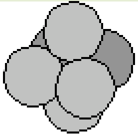
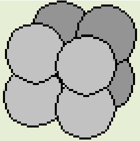
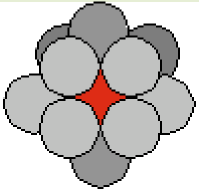
Table 1. Radius of the main ion A°

Element	Radius of the ion (Angstrom)
O	1,40
Si	0,42
Al	????
Fe	0,74
	0,64
Ca	+0,99
Na	0,97
K	1,33
Mg	0,66
Ti	
Mn	0,80

the vertices.

The shape of a polyhedron depends on the ratio between the ionic radius of the cation (Rc) and the ionic radius of the anion. The different possible shapes depending on the ratio of ionic radii are presented in the table below.

Table 2. Diferent possible shapes depending on the ratio of ionic

Rc/Ra ratio	Coordination Number	Geometry	Aspect of the polyhedron
<0,155	2	line	
0,155	3	triangle	
0,255	4	Tetrahedron	
0,414	6	Octahedron	
0,732	8	Cubic	
1,0	12	cubo-octahedron	

- **Determination of the crystal structure of minerals**

Calculation of molecules in a unit cell:

This calculation is done using the following formula:

$n=(v*d)/(1.66*m)$

n: number of molecules in a unit cell.

v: unit cell volume.

d: unit cell density.

m: molecular weight of the unit cell

Example: pyrite FeS_2, this mineral crystallizes in the cubic system;

M=55.847+2 (32.064)=119.975

V=a^3=(5.42)^3=159.55

D=4.99

So n= 4, we then have a face-centered unit cell.

2. *Diamond face centrée*

D 3.5 v 0.0454 nm3

Calculation of volumes

cube=a^3

quadratic=a^2.c

hexagonal=a^2 .c sin60°

rhombohedral=a^3 (1-cosα)^(1/2) (1+2cosα)^(1/2)

arthorombic=a.b.c

monoclinic=a.b.c sin(180- β)

triclinic=a.b.c √([cosα-cos(β+δ) [cos(β-δ)-cosα]])

- **The Main Minerals Of The Earth’s Crust**

We see that the most abundant elements are oxygen and silicon; the most abundant minerals will therefore be silicon oxides, known as silicates.

The quantity of minerals making up the earth's crust represented in the pie chart below. We see that only 8% of minerals are not silicates. We distinguish several families whose nature we will study.

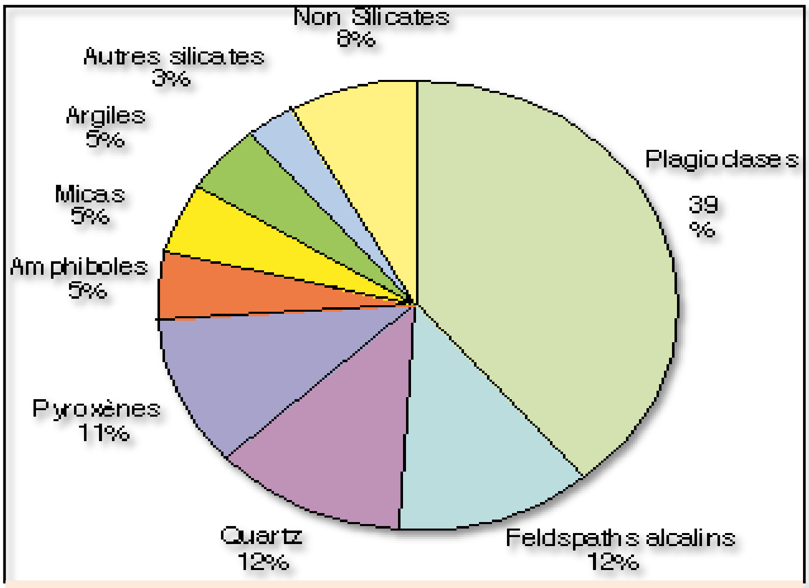
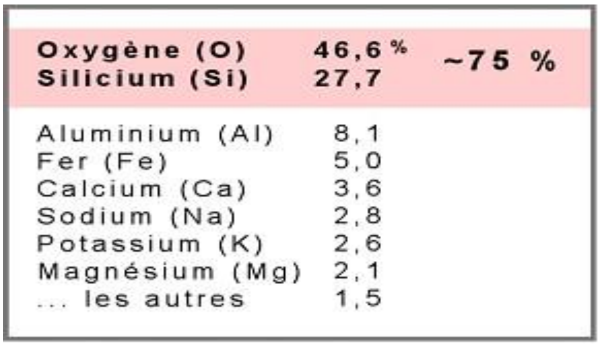


Figure 1. Abundant minerals making up the earth's crust

We see that only two elements, Si and O, account for almost three quarters (74.3%) of all materials. It is therefore not surprising that a group of minerals composed fundamentally of Si and O with a certain number of other ions and called silicates, alone makes up 95% of the volume of the earth's crust. Note that this distribution is only applicable to the earth's crust. We consider that the core is composed almost exclusively of iron and nickel, which is very different from what presented here. During the formation of the earth, light elements, such as oxygen and silicon migrated outwards, while heavier elements, such as iron, concentrated in the center.

Table 3. Abundant elements in earth's crust



Oxygène (O)	**46,6 %**	**~75 %**
Silicium (Si)	**27,7**	
Aluminium (Al)	8,1	
Fer (Fe)	5,0	
Calcium (Ca)	3,6	
Sodium (Na)	2,8	
Potassium (K)	2,6	
Magnésium (Mg)	2,1	
... les autres	1,5	

All silicates have a basic structure composed of Si^{4+} and O^{2-} ions. If we connect the centers of the oxygens, we obtain a volume which forms a tetrahedron, in the basic tetrahedron the silicon occupies the center of the tetrahedron, the calculation of the electric charges shows that a tetrahedron is negatively charged.

For purposes of simplification in the construction of models, we represent the basic tetrahedron in this way. In minerals, the charges must be neutral. There are two ways to neutralize the charges: link the tetrahedra together by their oxygens (tetrahedron-to-tetrahedron bonds), or add positive ions, such as irons, magnesiums, or potassium (metallic bonds).

2. Reminders Of The Structure Of The Atom And Chemical Bondings

2.1. Reminders of the structure of the atom

The main constituents of **atoms** are:

- The nucleus is made up of a **nucleons** and the **electron** gravitates around the nucleus while rotating on itself.

- The atom is electrically neutral and the mass of the atom is concentrated in the nucleus (the mass of the electron is negligible compared to that of the nucleus)

- The structure of the atom is called "lacunar" since the electron is very far from the nucleus. (radii: atom Ra = 5.10^{-2} nm and nucleus Rn = 5.10^{-7} nm)

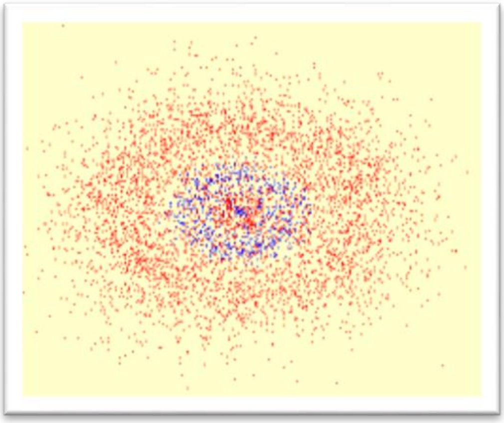


Figure 2. Electronic cloud at atom

- The electron does not move on a fixed and determined trajectory (probability of occupying a given region) it is the electronic **cloud**, which represents all the positions likely to be occupied by the electron

Noyau ≈ 10^{-15} m

Atome ≈ 10^{-10} m

- **Symbolic representation of the atom**

An atom can be represented symbolically by where:

- X is the symbol for the atom
- **A** is called the ***mass number*** and represents the number of **nucleons (**neutrons + protons**)** in the nucleus of the atom.
- **Z** is called the ***atomic number*** and represents the **number of protons** in the nucleus of the atom (equal to number of electron so, **Z gives also, the number of electrons** in the atom).
  - The difference A-Z therefore gives the number of neutrons in the nucleus

Example

1 - The carbon atom is represented by $^{12}_{6}C$, that is to say:

Z = 6 → 6 protons in the nucleus therefore 6 electrons.

A = 12 → 12 nucleons therefore 12 – 6 = 6 neutrons in the nucleus.

2 - The Sodium atom is represented by ${}^{23}_{11}Na$, that is to say:

Z = 11 → 11 protons in the nucleus therefore 11 electrons.

- A = 23 → 23 nucleons therefore 23 – 11 = 12 neutrons in the nucleus.

*** Characteristic mass of the atom**

*** Mass of the nucleus**

The nucleus of an atom is made up of nucleons of two types: Neutrons and protons so to calculate its mass, simply add the masses of the particles which constitute it using the following values:

$$\mathbf{m_{nucleus} = m_p * (number\ of\ protons) + m_p * (number\ of\ neutrons)}$$

$m_{nucleus}$ (Fe) = mp × (Z) + mn × (A - Z)

$m_{nucleus}$ (Fe) = $1{,}673.10^{-27} \times (26) + 1{,}675.10^{-27} \times (30) = 9{,}375.10^{-26}$ kg

- **Mass of electrons**

Electrons have a mass 2000 times lower than that of nucleons:

- **Mass of the atom**

We notice that the mass of an electron is very small compared to that of nucleons so the mass of the atom is concentrated in its nucleus. The masses of protons and neutrons are almost identical too, if we neglect the mass of electrons:

$M_{atome} \approx A \times mp$

2.2. CHEMICAL BONDINGS IN MINERALS

By bond we designate all the interactions involved in keeping the atoms linked together, thus forming stable molecules.

These bonds correspond to bond energies of the order of 50 kcal/mole; these are chemical bonds. They bring the atoms linked together at distances of 1 to 2 A°, if these atoms are not too large (atoms from the first 2 lines of the periodic table), we often distinguish the following three types of bond:

- Ionic bond;
- Covalent bond;
- Metallic bond.

- Van der Waals bond

a. Ionic bonding:

These are heteropolar bonds, that is to say between ions of opposite signs (e.g. Na^+ and Cl^-), they appear when atoms of very different electronegativity unite, in this case one of the atoms monopolizes a electron from the other atom. The molecule is then made up of 2 ions A+ and B- there is transfer of electrons from one atom to the other.

Ionic crystals are formed from the assembly of ions with opposite signs. Structures tend to achieve configurations corresponding to the minimum energy.

- There are purely ionic crystals such as fluorides and alkaline chlorides, we take halite (Na Cl) as a typical example. Example: the halite crystal: Such a crystal is formed from a regular stack of chloride ions Cl- and sodium ions Na+.

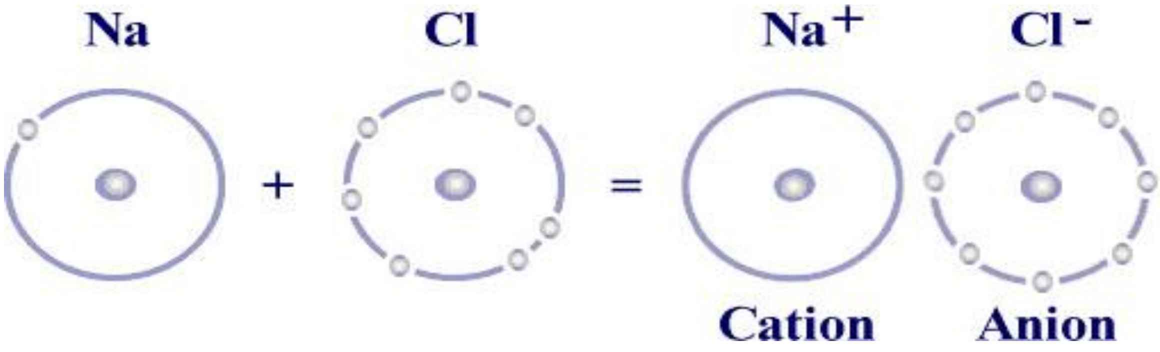


Figure 3. Example: Ionic bonding of the halite crystal

The crystal is stack of unit cell. The ions occupy the vertices of the cube, the middle of the edges, the center of the unit cell and the centers of the faces: we say that the structure is face-centered cubic.

Another example of ionic crystals: Ternary compound: CaTiO3 perovskite.

b. Covalent bonding:

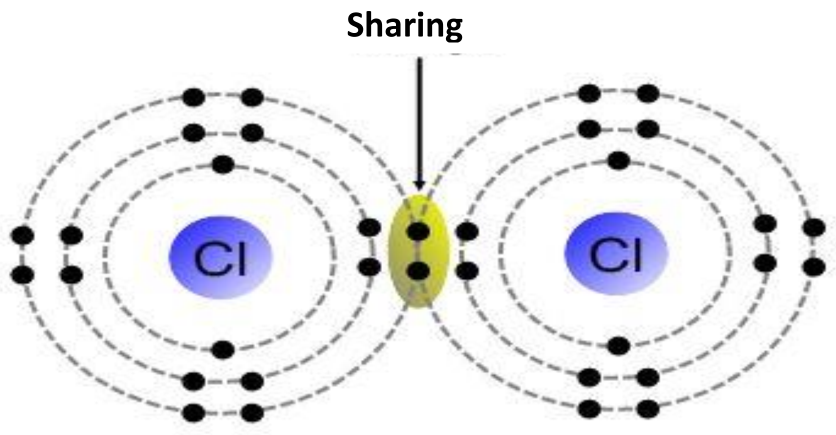


Figure 4. Example: Covalent bonding of Cl_2

They are also called homopolar or atomic bonds because they are established between atoms of similar electronegativity and not ionized. They can be described as the sharing of peripheral electrons of atoms, generally by forming electron pairs. The covalent bond is single or multiple depending on the number of electrons shared by the atoms.

Unlike the mode of arrangement found in ionic crystals, the number and location of the atoms surrounding a given atom in valence crystals are conditioned by the covalence of this atom.

In the diamond structure each atom is surrounded tetrahedrally by four other atoms; all atoms are **covalently** connected and all C-C bonds are equal.

By juxtaposing an infinity of patterns similar to that of Figure B1, we reproduce the three-dimensional crystal lattice of the diamond.

In graphite the carbon atoms are arranged in parallel planes, in each plane the atoms form a network of hexagons. In a plane, the C-C bonds are covalent and of the same length, between two parallel planes or sheets the bonds are weak,

Let's compare the diamond crystal to that of graphite:

Diamond	Graphite
• Very hard	• Fairly soft (malleable).
• Non-conductor of electricity	• conductor in the directions // to the leaflets.
• Non-lubricating	• Lubricant.
• Chemically inert	• Fairly active.

Diamond is denser than graphite, therefore more condensed, high pressure favors its formation (confirmed by geological observations). In the laboratory we obtain diamond from graphite under a pressure of around 95,000 atmospheres and a temperature of around 1900 K°

c. Metallic bonding:

It is characterized by the fact that all atoms release their valence electrons by becoming positive ions, while the free electrons circulate between these ions in an electron cloud format. This explains the electricity of metals.

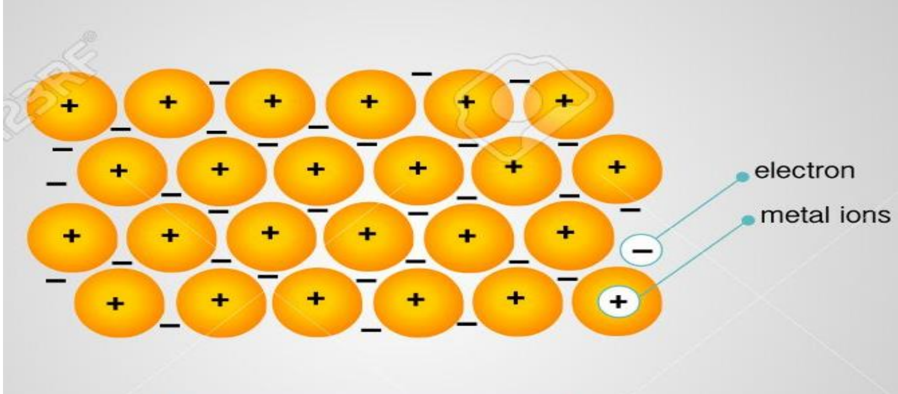


Figure 5. Schematic plan of Metallic Bonding

The metal crystals appears as a set of positive ions embedded in an electronic cloud which is distributed throughout the crystal; these electrons ensure the cohesion of the network of fixed ions.

The structure of the metal gives it a number of characteristic properties, which are:

- They form crystalline buildings of high symmetry (cubic, hexagonal).
- Compact or almost compact stacking of heavy atoms gives solids of high density.
- Thermal conductivity: the presence of the electronic cloud explains the high thermal conductivity of metals: if we heat a metal at a point, the kinetic energy of the electrons at this location increases, as the electrons can move throughout the crystal, the increase in temperature spreads quickly.
- Metals are malleable: they easily deform under the effect of mechanical stress.

d. Van der Waals bond

This type of bond is important in certain minerals intermolecular forces that are dependent on the distance between atoms or molecules. These forces arise from the interactions between uncharged atoms/molecules. This is a very weak bond that links neutral molecules and essentially unchanged structural units; The connection is made via small electronic charges.

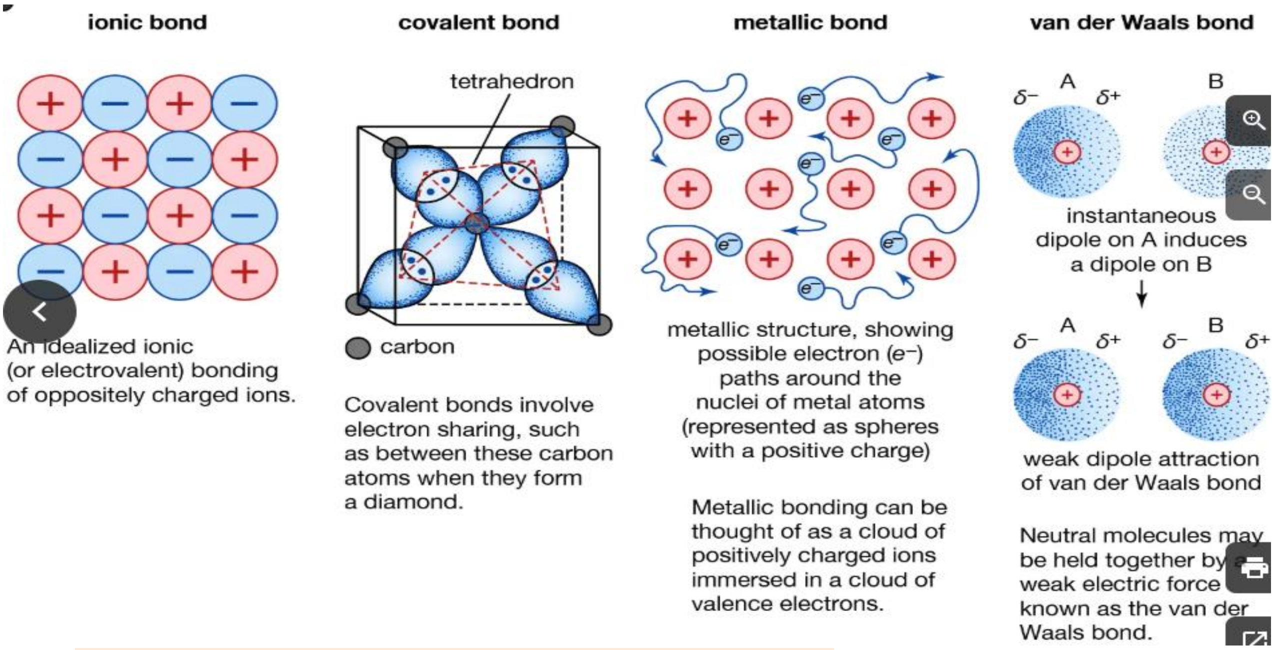


Figure 6. Chemical bonding in crystalline solids

V**an der Waals forces**, relatively weak electric forces that attract neutral molecules to one another in gases, in liquefied and solidified gases, and in almost all organic liquids and solids. The forces are named for the Dutch physicist Johannes Diderik van der Waals, who in 1873 first postulated these **intermolecular** forces in developing a theory to account for the properties of real gases. Solids that are held together by van der Waals forces characteristically have lower melting points and are softer than those held together by the stronger ionic, covalent, and metallic bonds.

4. Definition Of Coordination, Isotypism, Isomorphism and Polymorphism

4.1. Coordination and cationic substitutions (The most common substitutions)

The vertices of the polyhedron then define sites in which the cations are housed. The same site can be occupied by cations of several types if the ionic radii do not differ too much. We thus define substitutions, which are the replacement of one cation by another. Classically, Si^{4+} is replaced by Al^{3+} and Ti^{4+}, Mg^{2+} by Fe^{2+} and Mn^{2+}, Na^{+} by Ca^{2+} and K^{+} by ion (Ba^{2+}, NH^{4+}, Cs^{+}).

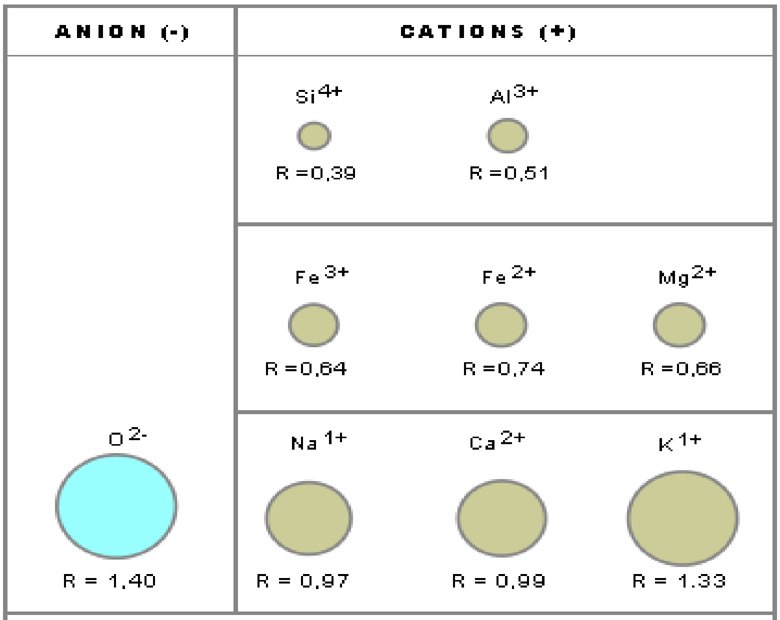
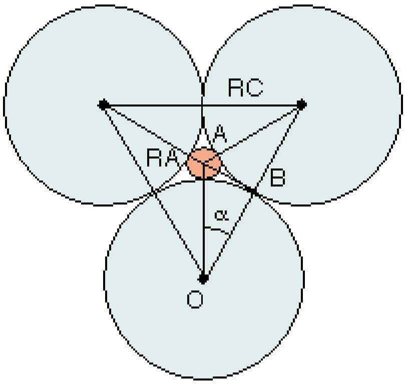


Figure 7. Ions radius (in Angstrom)

Cations occupy sites in minerals formed by oxygen. Depending on the size, the ions occupy certain sites, tetrahedrons, octahedrons, etc. Two ions can substitute each other if they have relatively similar radii. The most common substitutions are:

- $Si4^{+}$ by $Al3^{+}$ in tetrahedral position. But be careful, the radius of $Al3^{+}$ also allows it to occupy octahedral sites. Si^{4+} can also be replaced by Fe^{3+}, Ti^{4+}
- Mg^{2+}, Fe^{2+} and Mn^{2+} can substitute each other
- Ca^{2+} and Na^{+} can substitute for each other

K+ cannot replace any of the previous cations, but can replace other much less common cations: Sr2+, Rb+ in particular.



OA cos (alpha) = OB

avec : OA = RA+RC et OB = RC

(RA+RC) * cos (alpha) = RC

RA = RC (1 - cos(alpha))□

et comme apha = 30°

RA = 0,155 * RC soit 15,5% de RC

Even though each mineral has a defined chemical composition, some variations are allowed. Thus, there may be substitution of certain ions for others. For example, the mineral olivine has the composition $(Fe, Mg)_2\ SiO_2$, which means that the proportion between iron and magnesium can vary. Ion substitutions in inerals are largely controlled by the size and charge of the ions, which is illustrated in the following diagram. Thus, it will be easy to make substitutions of ions of similar size and charge, such as substituting iron (Fe) for magnesium (Mg), or sodium (Na) for calcium (Ca), but it will be more difficult to substitute potassium (K) or oxygen (O) for aluminum (Al).

4.2. COMPOSITION AND STRUCTURE OF MINERALS

4.2.1. Stoichiometry vs non-stoichiometry

In a compound body that contains two elements, if the proportion of these two elements is identical to that of the formula group, we say that the compound is stoichiometric. If the defects change the composition of the crystal, the compound is non-stoichiometric.This is for example the case of iron oxide FeO. Depending on experimental conditions, the iron atom deficit can go up to $Fe_{0.862}$ O. The composition of this iron deficient oxide is expressed by the formula Fe_{1-x} O (wüstite). To maintain electroneutrality, part of the Fe^{2+} ions is replaced by Fe^{3+}

Figure 8. Cristals Photos of non-stoichiometric (pyrrhotite 3) and stoichiometric (Quartz 1 and Talc 2) minerals.

Le quartz : SiO_2

Le Talc : $Mg_3Si_4O_{10}\ (OH)_2$

La pyrrhotite : $Fe_{1-x}S$, X variable continue (x = 0 to 0.2)

The rare stoichiometric FeS is known as the mineral *troilite*

4.2.2. **Isotypism :** Two mineral species are **isotypes** when they have distinct chemical compositions but similar structural formulas, they belong to the same crystal system and the coordination polyhedra involved in the two structures are identical or comparable. Ex *halite*: NaCl; and *sylvine:* KCl

Are isotypes and they both belong to the cubic group at centered faces.

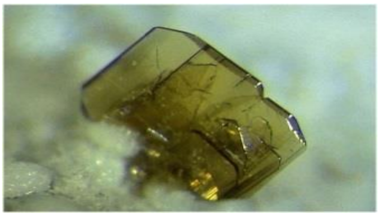
3.2.3. Isomorphism (Solid Solutions) and H*eteromorphism*

Two mineral species are isomorphic, if they are isotypes, made up of cations and anions of neighboring ionic radii to consider their syncrystallization into mixed crystals. The two species form solid solutions. Ex: peridots whose composition varies from a magnesium term (Mg_2SiO_4) forsterite with an iron-bearing term (Fe_2SiO_4) fayalite. The intermediate term being olivine.

Pôle magnésien (Forstérite) Mg_2SiO_4

Olivine ($(Fe_x Mg_{1-x})_2SiO_4$)

Pôle ferrifère (Fayalite) Fe_2SiO_4



* Conditions for replacements or isomorphic substitutions

Isomorphic substitutions will only be possible if certain conditions are met.

a) The ionic radii must be close, the difference between the ionic radii must not exceed 15%. K and Na cannot substitute each other because the ionic radius of K = 1.33 and the ionic radius of Na is 0.97 (the difference between the 2 ionic radii is greater than 15%). b) The coordination polyhedra must have identical shapes, as does the coordination.

c) The valency and electronic structure must be similar. If the valences are different, the excess or deficiency of charges must be compensated by another replacement restoring the balance it is a heteromorphic replacement.

Heteromorphism : Ex Plagioclase series ; albite ($NaSi_3AlO_8$) and anorthite ($CaSi_2Al_2O_8$).Ca^{2+} - Na^+ and Si^{4+}-Al^{3+}

3-pole isomorph	Grenats (Fe^{2+}, Mg^{2+}, Mn^{2+})$_3$ $Al_2[SiO_4]_3$

Albite oligoclase andésine labrador bytownite anorthite

0 10 30 50 70 90 100

$NaAlSi_3O_8$ $CaAl_2Si_2O_8$

$Nax\ Ca1\text{-}x\ Al2\text{-}xSi_2\text{+}XO_8$

Avec $0<x<1$

Coupled substitutions Na-Si ⟺ Ca-Al

d) Temperature and pressure play an important role. Some Isomorphic replacements are complete at high temperature and high pressure, but partial at low temperature and low pressure. Ex sodipotassium alkali feldspars where the decrease in temperature causes the formation of two phases: perthites.

Depends on substitution possibilities (Goldschmidt rules

Mg2+ Fe2+ Mn2+ Fe2+ Mn3+ Fe3+ Sr2+ Ca2+ Sr2+ Ca2+ Cu2+ Zn2+ Ca2+ Mn2+ Mg2+ Mn2+ Sb2+ As2+ Ba2+ Sr2+ Pb5+ As5+

Almandin	$Fe_3^{2+}Al_2[SiO_4]_3$	
Pyrope	$Mg_3^{2+}\ Al_2[SiO_4]_3$	
Spessartine	$Mn_3^{2+}\ Al_2[SiO_4]_3$	

Depends on substitution possibilities (Goldschmidt rules).

4.2.3. **Polymorphism** (minerals stability in PT conditions)

Two or more mineral species are said to be polymorphic if they have the same chemical composition but different crystal structures. This change in shape is linked to variations in temperature and pressure.

Ex: carbon C

When it crystallizes in the cubic system, it gives diamond

And when it crystallizes in the hexagonal system, it gives graphite.

When they concern simple elements such as, C, S, etc., they are called allotropes

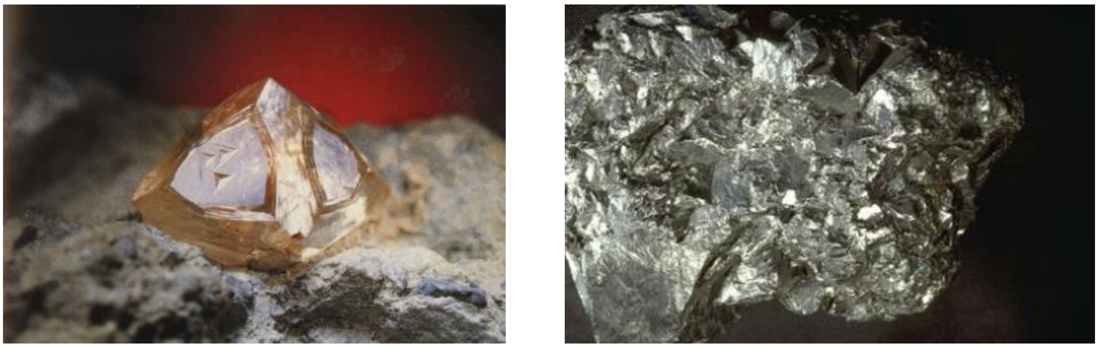
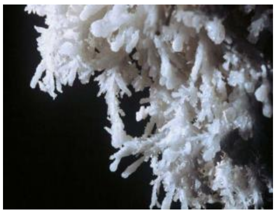


Figure 9. Carbon polymorph (Diamond and Graphite).

$CaCO_3$	calcite	Rhomboédrique	aragonite	orthorhombique
				
ZnS	blende	cubique	wurtzite	hexagonale
Al_2SiO_5	disthène	triclinique	Andalousite sillimanite	Orthorhombique quadratique
FeS_2	pyrite	cubique	marcassite	Orthorhombique
TiO_2	rutile	quadratique	Anatase Brookite	Quadratique orthorhombique
SiO_2	quartz-α	Rhomboédrique	quartz-β tridymite cristobalite Coesite stishovite	hexagonal Hexagonal Cubique à quad. Monoclinique quadratique

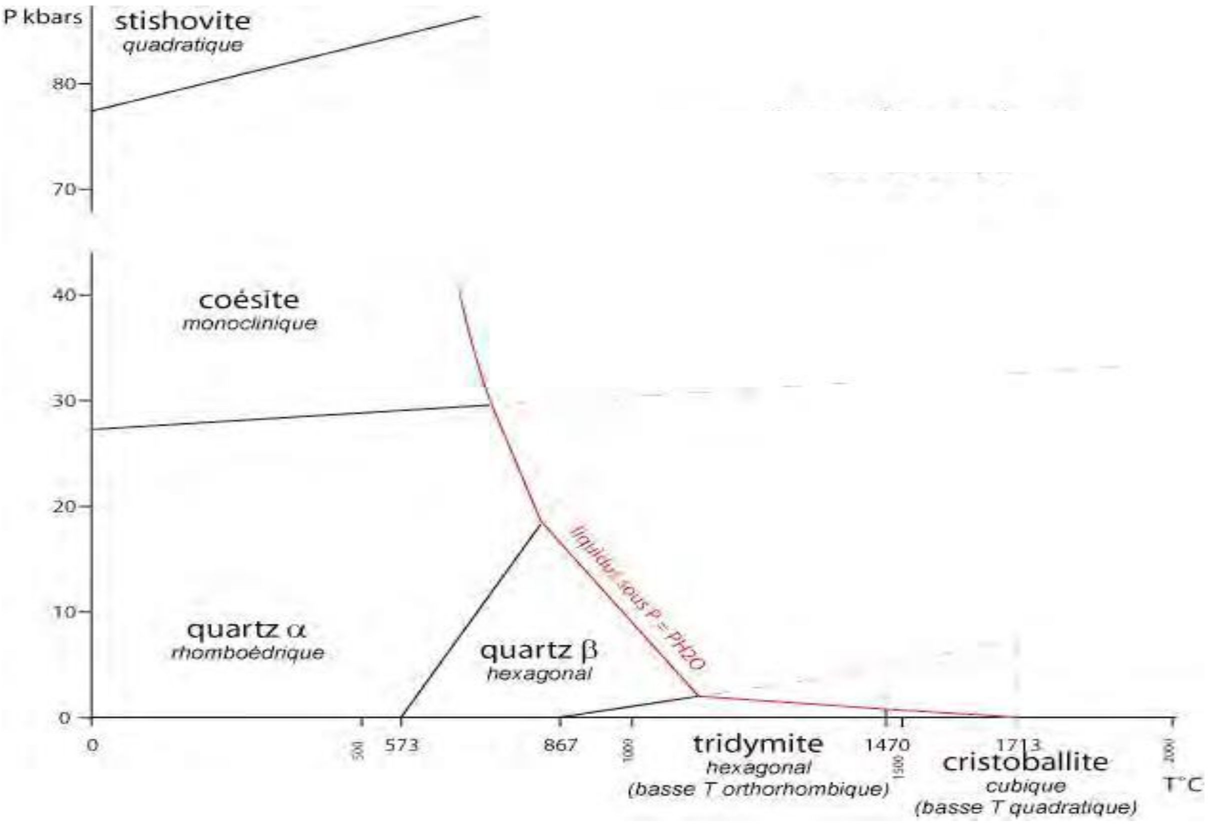


Figure 10. SiO_2 Polymorphs

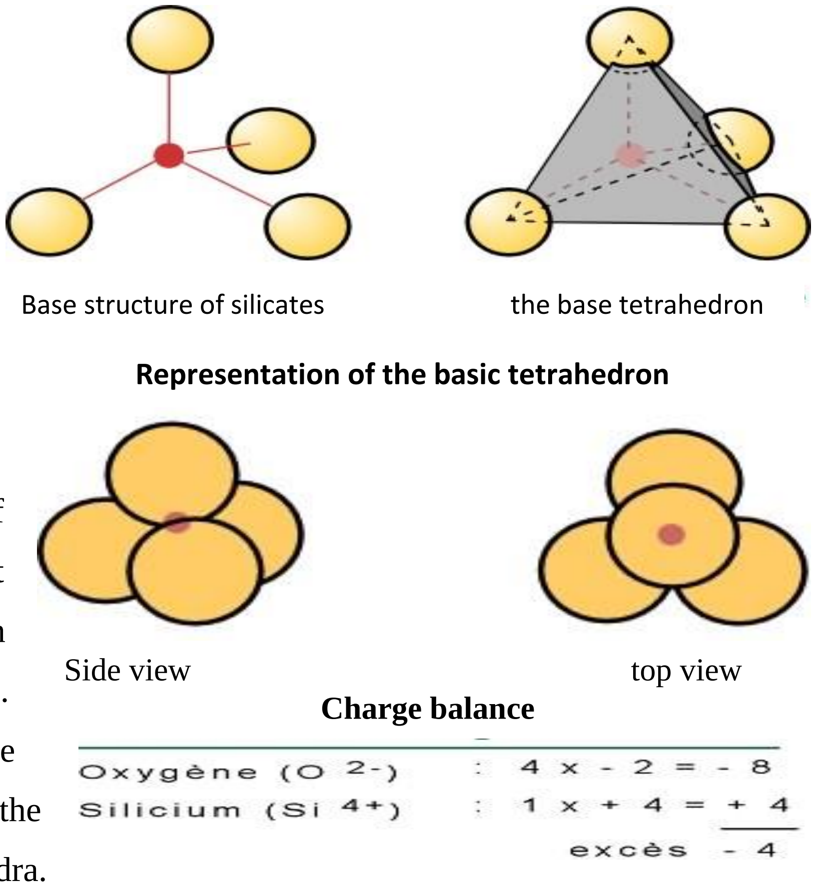
Chapter II

Mineral's Classification

II.1. SILICATES MINERAL SPECIES

Silicates, nearly 600 species, constitute .with silica approximately 95% by weight of all the minerals forming the earth's crust and ± 100% of the mantle, hence their extreme importance.

The Rc/Ra ratio of Si^{4+} and O^{2-} ions shows that the coordination polyhedron of silicates is a tetrahedron. Silicates can therefore be described as resulting from the stacking of tetrahedra. Depending on the mode of arrangement of the $[SiO4]^{4-}$ tetrahedra, a structural classification of silicates is established.



Base structure of silicates

the base tetrahedron

Representation of the basic tetrahedron

Side view

top view

Charge balance

Oxygène (O^{2-}) : 4 x - 2 = - 8

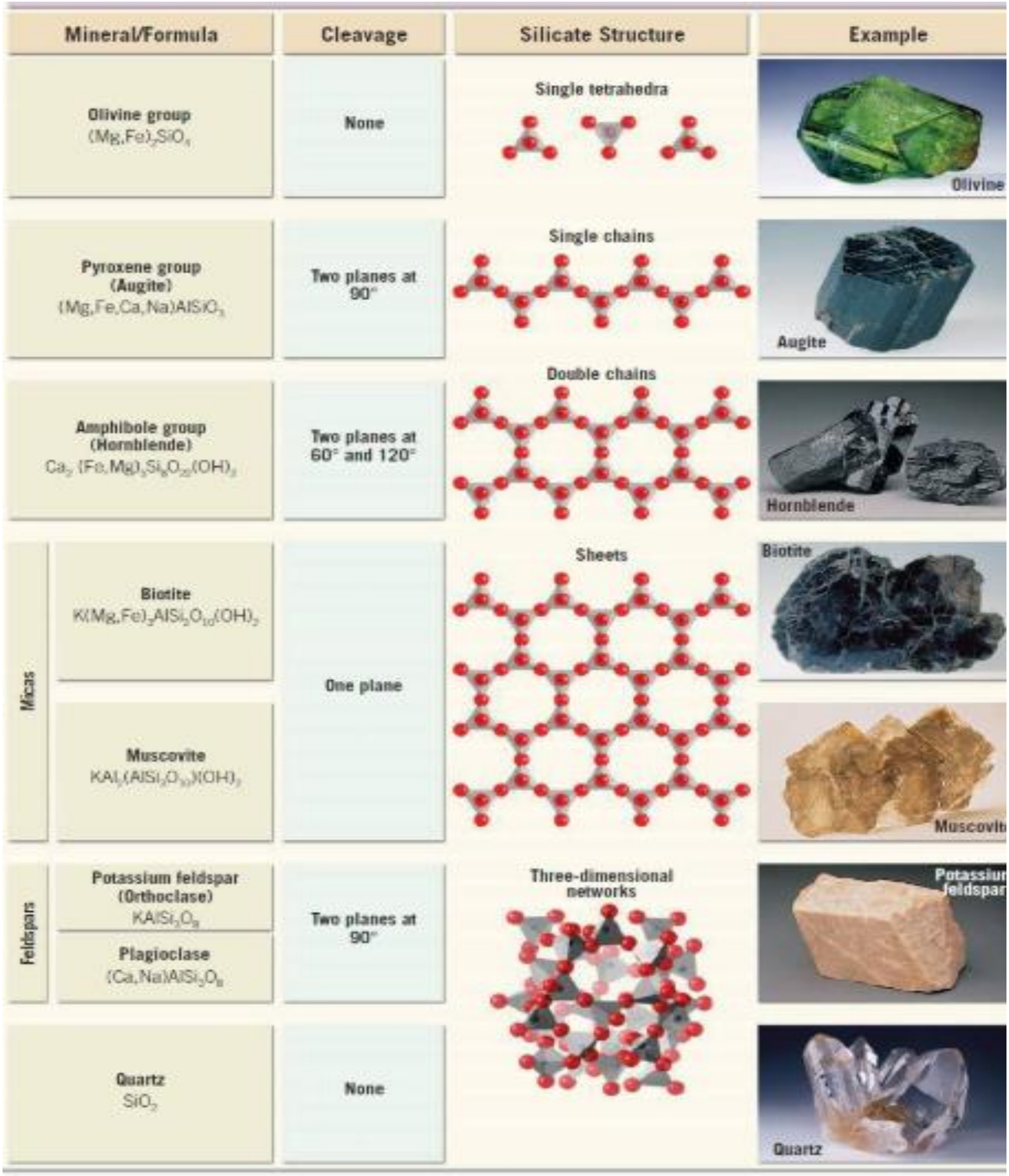
Silicium (Si^{4+}) : 1 x + 4 = + 4

excès - 4

Figure 11. Arrangement of the $[SiO_4]^{4-}$ tetrahedra of SiO_2

It is from these four basic structures, isolated tetrahedron, single chain, double chain and layer, that silicates will be formed. The groups of olivines, pyroxenes, amphiboles and micas will be formed by the addition of positive metal ions such as iron, magnesium, calcium, potassium, etc., which will neutralize the structure (metallic bond).

Table 4. Common Silicate minerals and minerals



	Mineral/Formula	Cleavage	Silicate Structure	Example
	Olivine group $(Mg,Fe)_2SiO_4$	None	Single tetrahedra	Olivine
	Pyroxene group (Augite) $(Mg,Fe,Ca,Na)AlSiO_3$	Two planes at 90°	Single chains	Augite
	Amphibole group (Hornblende) $Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2$	Two planes at 60° and 120°	Double chains	Hornblende
Micas	**Biotite** $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	One plane	Sheets	Biotite
	Muscovite $KAl_2(AlSi_3O_{10})(OH)_2$			Muscovit
Feldspars	**Potassium feldspar (Orthoclase)** $KAlSi_3O_8$	Two planes at 90°	Three-dimensional networks	Potassiu feldspar
	Plagioclase $(Ca,Na)AlSi_3O_8$			
	Quartz SiO_2	None		Quartz

In highly **polymerized silicates** (chains, layers, frameworks), silicon atoms are often partially replaced by aluminum. We then encounter a certain proportion of [AlO4] tetrahedra among the [SiO4] tetrahedra. We then speak of alumino-silicates. 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 in the form of (OH) or H2O. Silicates can be classified according to the different modes of linking tetrahedra $[SiO_4]^{4-}$.

1.1. Nesosilicates: (nésos = île) isolated tetrahedra $[SiO_4]^{4-}$

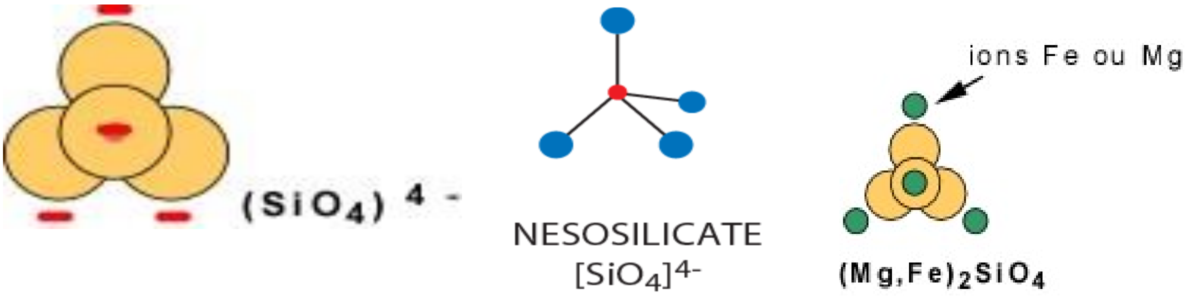


Figure 12. Structure of nesosilicates

In the case of isolated tetrahedra, the structure is charged at -4, as seen above in the calculation of charges; the red lines here illustrate the negative poles corresponding to the 4 oxygens. The $[SiO_4]^{4-}$ groups do not share (bridging) oxygens and are linked together by cations. Crystal system of high symmetry, isometric morphology and weak cleavage properties.

Case 1: Bonds of tetrahedra isolated by metal ions: olivine. Several isolated tetrahedra are united by their four negative poles thanks to positive Fe or Mg ions; it is the mineral olivine (ferromagnesian silicates). The proportion of iron and magnesium may vary.

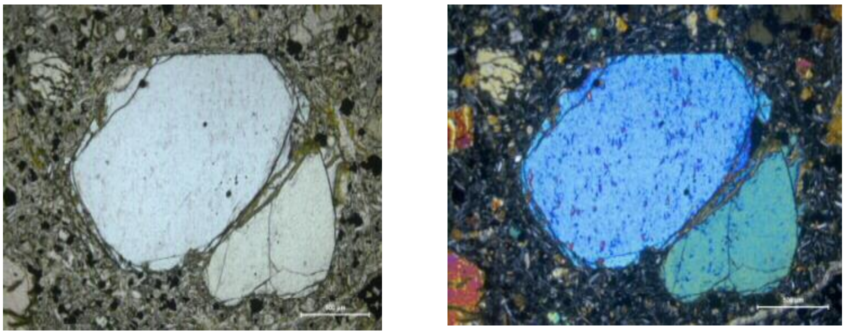


Figure 13. Olivine observation in LPNA et LPA

Other examples:
Olivine or Orthorhombic Peridots $(Mg, Fe)_2 SiO_4$

Garnet group

They form complex solid solutions with the general formula:

$(SiO_4)_3 Y^{3+} X^{2+}$

With $Y^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}$

And $X^{2+} = Fe^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}$

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

	Al^{3+}	Fe^{3+}	Cr^{3+}
Fe^{2+}	Almandin		
Mg^{2+}	Pyrope		Hanleite
Ca^{2+}	Grossulaire	Andradite	Ouvarovite
Mn^{2+}	Spessartine	Caldérite	

Table 5. Physical properties of aluminous garnets

Species	Color	Hardness	Density
Almandin	Pink to reddish-brown	7	4.25
Pyrope	Garnet	7 à 7.5	3.51
Grossulair	Colorless, pinkish to greenish-yellow	6.5	3.53
Spessartine	Yellow to reddish-brown	7 à 7.5	4.18
Andradite	Green to brownish-black	7	3.75
Ouvarovite	Emerald green	7	3.77

Aluminous garnets and andradite are the most common. Garnets all crystallize in the cubic holohedral m3m 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 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 granitic pegmatites.

Andradite in contact metamorphism rock.

Ouvarovite in chromiferous serpentinites.

Quadratic Zircon Zr SiO_4

Nésosubsilicates : Présence d'O n'appartenant pas aux tétraèdres Al_2 [O SiO_4]

Topaze, $Al_2SiO_4(F,OH)_2$

Sphène CaTiOSiO4

Andalusite Orthorhombic SiO_2 Al_2O_3

Orthorhombic Sillimanite SiO_2 Al_2O_3

Kyanite Triclinic SiO_2 Al_2O_3

Staurotide Orthorhombic Fe SiO_2 Al_2O_3 $(OH)_2$

Spinels (family) Cubic $MgAl_2O_4$

Monoclinic Titanite $CaTiO_2$ SiO_3

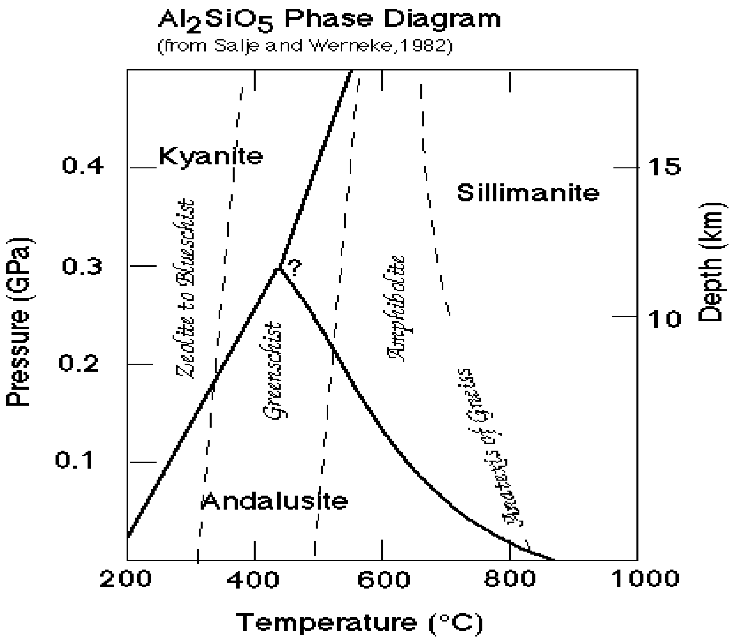
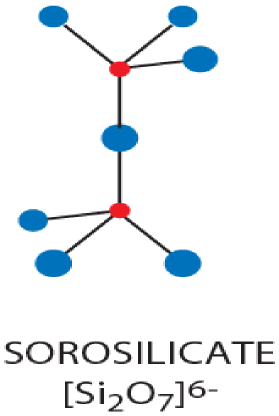


Figure 14. Al_2 Si_3O_5 Phase diagram

1.2. **Sorosilicates:** tetrahedra grouped in pairs $[Si_2O_7]^{6-}$ ☐ Silicates with pairs of tetrahedrons ☐ Sharing a bridging oxygen. Dieric framework. [The polymerization of tetrahedra by groups 2 leads to the formation of sorosilicate.



Silicates with this structure are very rare in nature. Practically, only melilites and hemimorphite are found. However, when there is an excess of oxygen compared to Si, the sorosubsilicate family stands out:

sorosilicates vrais Ex : Orthorhombic Hemimorphite Zn_4 Si_2O_7 $(OH)_2$ H_2O mélilite $Ca_2(Mg, Al)[Si, Al)_2O_7$

- **sorosubsilicates** Ex : Lawsonite Orthorhombic Ca Al_2 Si_2O_7 $(OH)_2$ H_2O
- **Sorosilicates à fonctions complexes**

Epidotes: Minerals in this group exhibit both (Si2O7) and (SiO4) functions as well as additional oxygen ions not bonded to silicon. We distinguish :

- Zoisite $(Si_2O_7)(SiO_4)O(OH)Al3Ca2$

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

- Pistachite $(Si_2O_7)(SiO_4)(OH)Ca_2FeAl_2O$

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

- Piemontite $(Si_2O_7)(SiO_4)O(OH)(Al, Fe3+, Fe2+, Mn2+)_3(Ca, Ce, La, Y3+)_2$ It is a variety which contains manganese and which crystallizes in the monoclinic system.
- Allanitis or orthotis $(Si_2O_7)(SiO_4)O(OH)(Fe^{3+}, Fe^{2+})_3(Ca, Ce, La,)_2Al_2O(OH)$

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 found in rocks of low regional metamorphism. Allanite found in acidic eruptive rocks: granites, granodiorites and pegmatites. Product of hydrothermal alteration of alumino-calcium silicates (feldspar, hornblende)

1.3. **Cyclosilicates:** tetrahedra in rings of 3, 5, 6 or more $(Si_3O_9)^{6-}$ $(Si_4O_{12})^{8-}$ $(Si_6O_{18})^{12-}$ Isolated rings connected by cations.

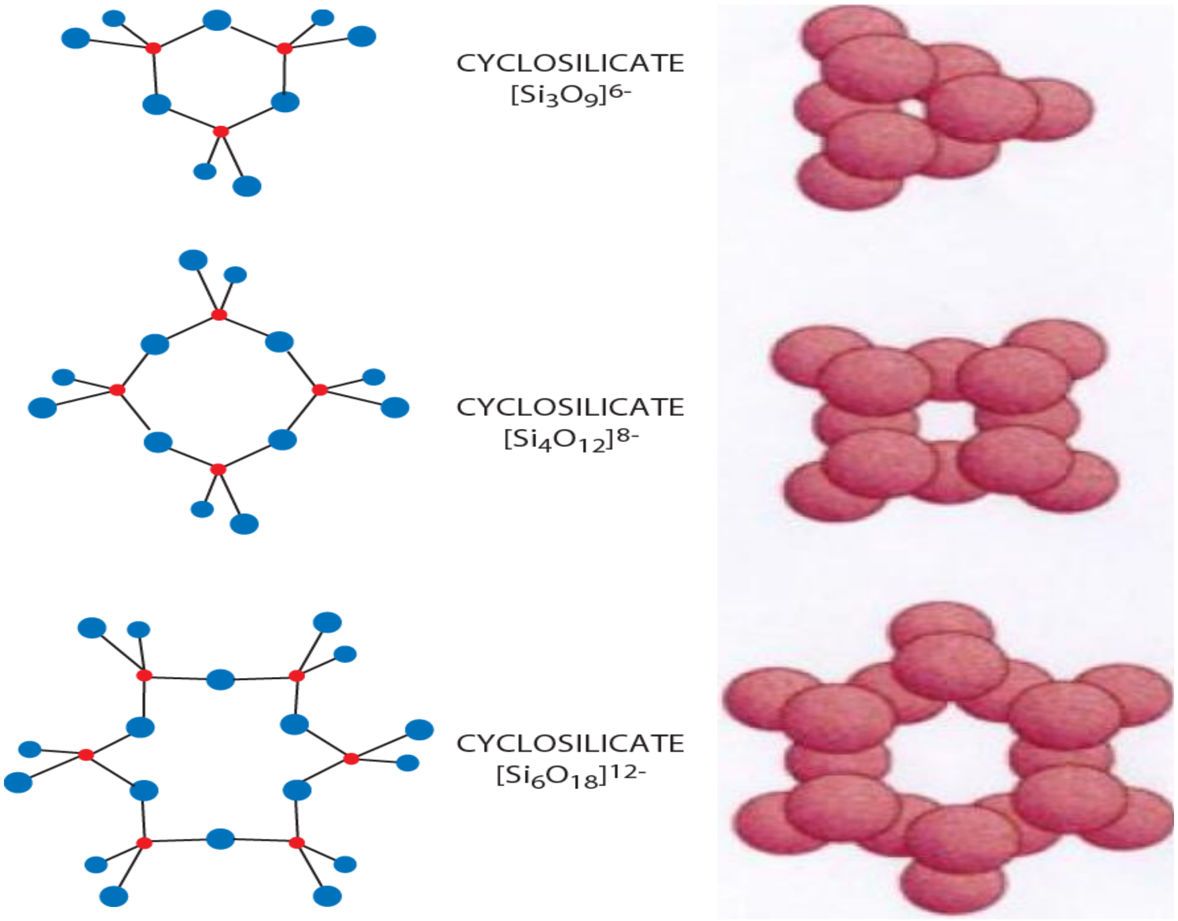


Figure 15. Structure of cyclosilicates

The polymerization of tetrahedra by groups 3,4 and 6 leads to the formation of cyclosilicates $[Si_3O_9]$ $[Si_4O_{12}]$ $[Si_6O_{18}]$

- Crystal systems are rhombohedral, quadratic and hexagonal.

Ex: **Beryl group**; Hexagonal $Be_3Al_2\ (SiO_3)_6$. It is the most widespread mineral containing beryllium. Beryl with the formula $(Si_6O_{18})\ Be_3\ Al_2$ crystallizes in the hexagonal system.

Beryl has a prismatic appearance. It 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 gems in high demand (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 metasomatosis in a context metamorphic (e.g. Siberian emeralds), or sedimentary (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.

The tourmaline group : Its formula is as follows:

[$(Si_6O_{18})(BO_3)_3(OH, F)_4$]$Al_6 Y_3$ Na.

Rhombohedral , 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, colored elbaite pink or blue. 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 it:

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.

Cordierite group; Of formula (Fe, Mg)2 Al4Si5O18

it crystallizes in the system Orthorhombic, pseudo-hexagonal, 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 colorful: 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 pinite

Deposit: cordierite is common in rocks of general metamorphism (gneisses, granulites, and migmatites) in rocks of contact metamorphism (schists and corneals) but also in igneous rocks (pegmatites and anatexia granites).

1.4. INOSILICATES:

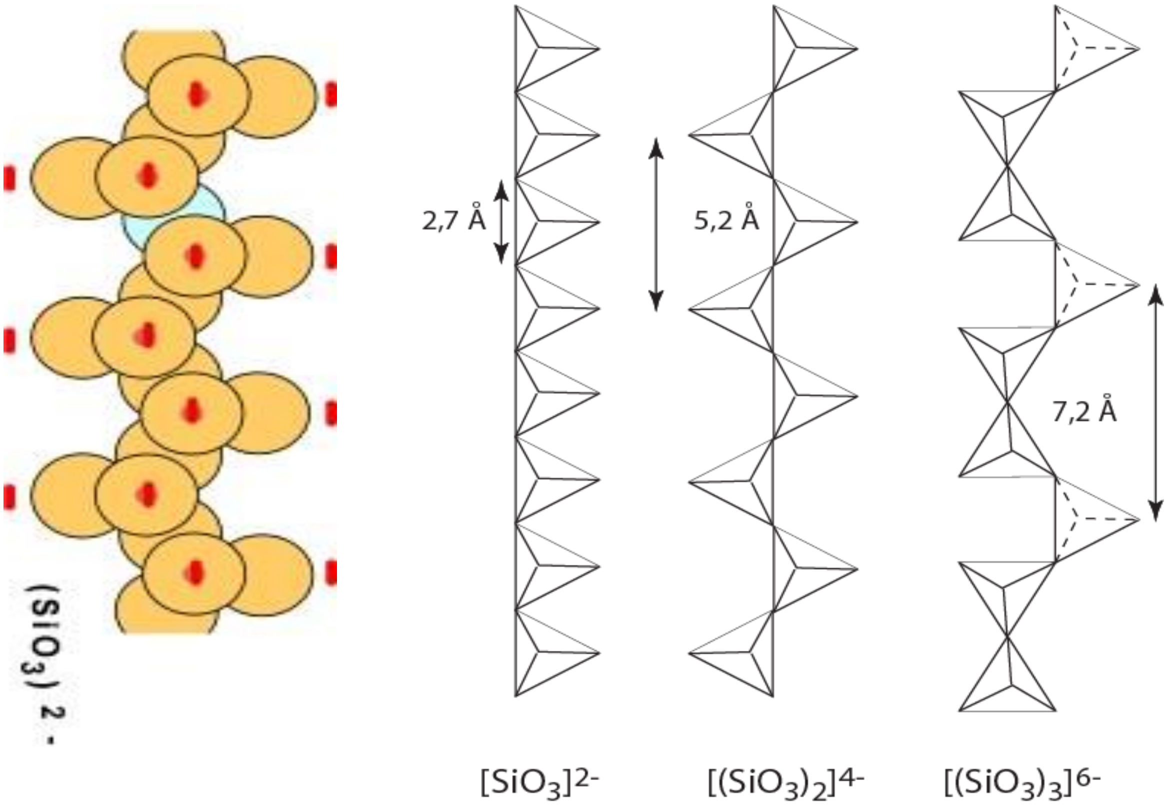
(Inos = fibre) single chain tetrahedra and double chain tetrahedra

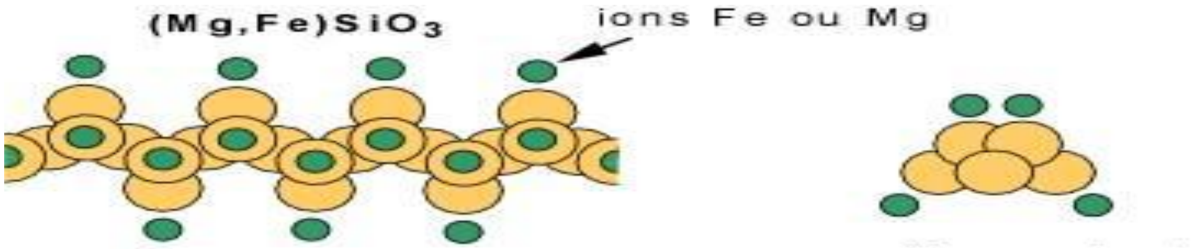
When each tetrahedron shares an oxygen, we obtain a simple chain of tetrahedra. The result is that for each tetrahedron 2 negative charges have been neutralized. The formula is $[Si_2O_6]^{4-}$ (**pyroxenes**).When two single chains unite through their oxygens to form double chains, we obtain a structure with the general formula: $[Si_4O_{11}]^{6-}$ with the presence of OH^- **(amphiboles**)

1.4.1. Pyroxenes :

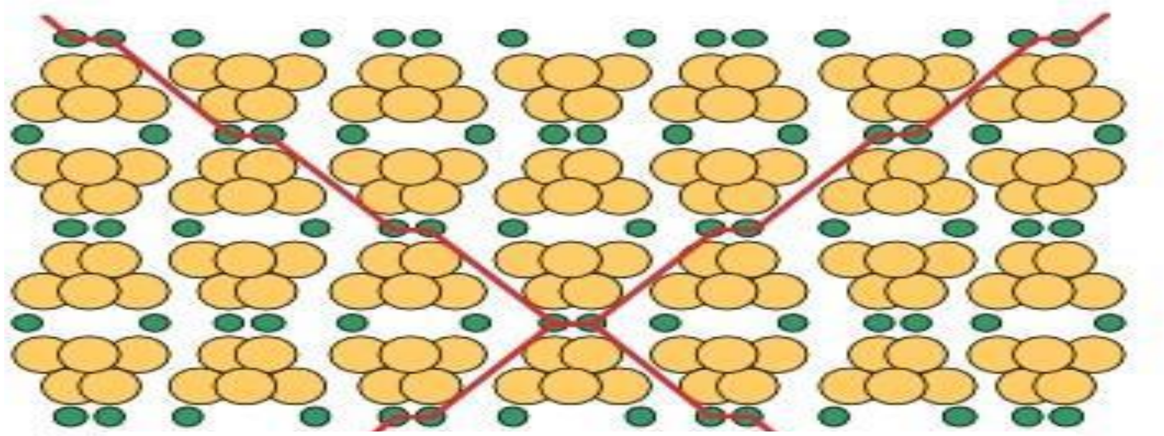
☐ Elongation of the crystals following the direction of the Si-O bond. When each tetrahedron shares an oxygen (in blue in the following diagram), we obtain a simple chain of tetrahedra. The result is that for each tetrahedron two negative charges have been neutralized and two others remain to be neutralized (the red lines); the structure is loaded at $^{-2}$. In pyroxenes, the chains are elongated along the c axis and their period is 2 tetrahedra, hence their formula $(Si_2O_6)_{4-}$

The general formula for pyroxenes is written as follows:





plan view **end view**



Several simple chains linked by metal ions

end view

Figure 16. Structure of inosilicates

$W_{1-*p}(X,Y)_p[(Si,Al)O_3]_2$ $<p<1$

W = Ca, Na, Li (gros cations)

X = Fe, Mg, Mn (moyens cations)

Y = Al, Fe, Ti (petits cations

Linking of simple chains by metal ions: pyroxenes. Around a simple chain, the available positions for iron and magnesium ions are at the periphery and at the top of the chain (see above). Here again, the proportion of iron and magnesium varies. The end view of a simple chain shows the position occupied by iron and/or magnesium ions, at the top and on the periphery. These ions join several chains, shown here again at the end, to form pyroxenes.

The bonds provided by metal ions, iron or magnesium, are weaker than the bonds provided by the sharing of oxygen between the poles of tetrahedra. This is what is responsible for the existence of two planes of weakness (red lines) at right angles. These planes of weakness correspond to the divide.

Two cleavage planes, 90° from each other, therefore characterize pyroxenes.

Orthopyroxenes (family) Orthorhombic $(Fe, Mg)_2\ Si_2O_6$

Clinopyroxenes (family) Monoclinic $(Ca, Mg)_2\ Si_2O_6$

Pyroxenes form a family of minerals which have the following characteristics:

- elongated prisms. The cross sections are generally octagonal with 4 sides more developed than the others. In longitudinal section, the sections are rectangular, slightly elongated
- Two traces of cleavage at approximately 90°, visible in the basal sections. In the longitudinal sections, only a single trace of cleavage is observed
- The relief is strong

Figure 17a. Ortho Pyroxene in polarized light. Note the octagonal shape of the section.

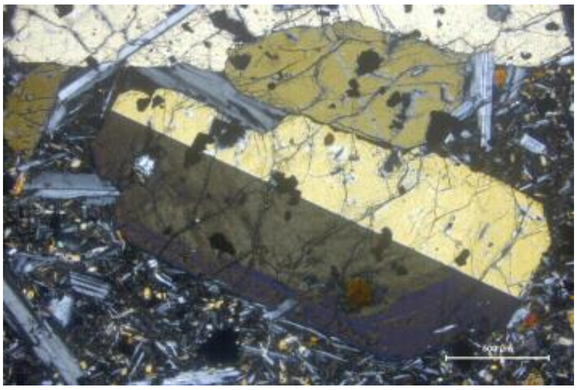


Figure 17b. Same section in polarized and analyzed light. Note the simple twin

- Birefringence is average (gray to yellow hues) in the case of othopyrixenes, bright (second order hues) in the case of clinopyroxenes
- The extinction angle is 0° in the case of orthopyroxenes, different from 0° in the cases of clinopyroxenes
- Possible presence of simple or hourglass twins
- possible presence of “fishbone” exsolutions

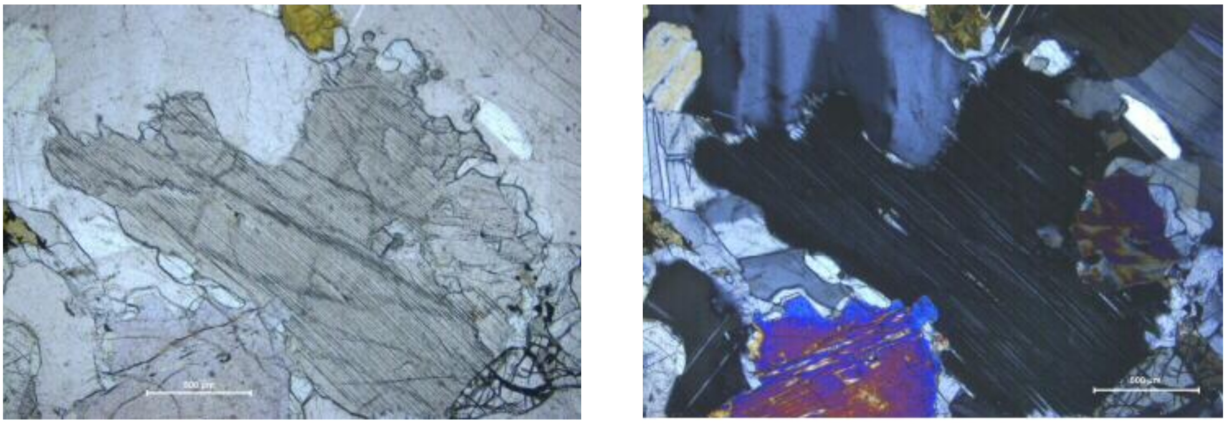


Figure 18. Clinopyroxene in polarized light and analyzed polarized light. Note the extinction angle, which is of the order of 45° in this case

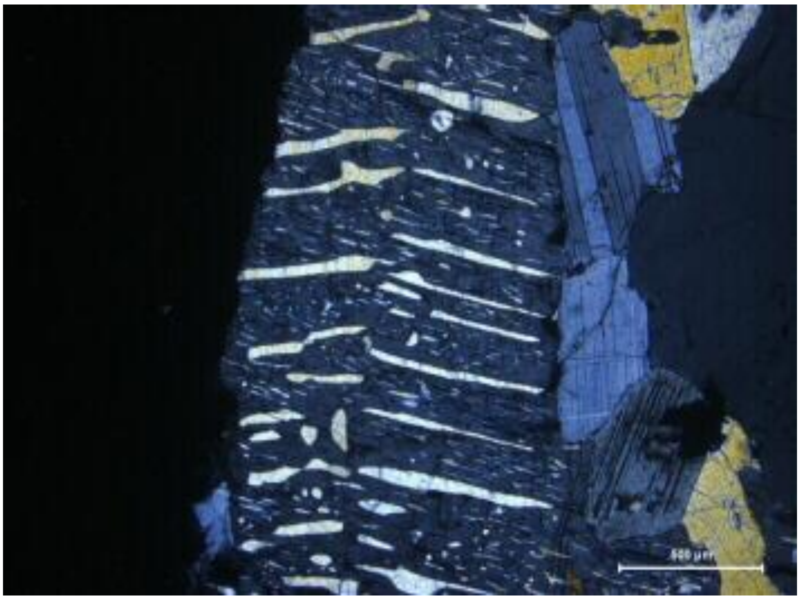


Figure 19. "Fishbone" exsolution of orthopyroxene in clinopyroxene

1.4.1.1. ORTHO-PYROXENES (OPX)

The OPX form a solid solution from a magnesium term *enstatite* of formula **$Mg_2Si_2O_6$** to the iron term ortho-*ferrosillite* of formula $Fe_2Si_2O_6$. The most common intermediate term is: *hypersthene*

Crisp OPX crystals are rare. Most often, these pyroxenes appear in fibrous, lamellar or compact masses.

Color: Magnesian terms are light colored, gray, pale green, yellowish white, sometimes light brown. Under the microscope, they are virtually colorless in LN. The extreme iron terms are greenish black or brownish. Those are the intermediate terms that are most often encountered in rocks.

Hardness is between 5 and 6 and density ranges from 3.1 to 3.5

Alteration: OPX weathers into serpentine or talc for the terms magnesiumians.

Deposit: OPX are common in basic and ultrabasic rocks (gabbros, norites, pyroxenolites, and peridotites). They are rarer in metamorphic rocks. They are associated with olivine, serpentine and magnetite.

1.4.1.2. CLINO-PYROXENES (CPX)

In the CPX Ca or Na (large cations) will occupy the W site. The pyroxenes are then calcic or sodium and they crystallize in the monoclinic system.

1.4.1.2.1. Calcium monoclinic pyroxenes

These pyroxenes always contain a little Fe and Mg and therefore classified according to the relative values of Ca, Mg, and Fe in the triangular diagram of POLDERVAART and HESS (1951). We thus distinguish:

The diopside CaMg Si_2O_6,

Hedenbergite Si_2O_6 CaFe

Augite Ca (Fe, Mg, Al, Ti) Si_2O_6

- **The augite**: is the most widespread mineral, it can be ferric, titaniferous and even contain a little sodium (Na), we then say that it is aegyrinic augite. Generally well crystallized in stocky prisms of octagonal sections. Its color varies from green-brown to black.

Conchoidal breakage. Clear divisions. Translucent to opaque. Vitreous sheen. Augites of volcanic origin often show an hourglass-shaped twin in LM. The diallage is a variety of augite with additional cleavage 110.

Hardness = 5 to 6 and Density = 3 to 3.6

Deposit: augite is the most common mineral in basic plutonic rocks (gabbros) and volcanic rocks (dolerites and basalts), but also in ultrabasic rocks (peridotites)

Alteration: augite weathers into uralite. Uralitization is the transformation of pyroxenes into green hornblende in association with pistachite and chlorite when the degree of alteration is high.

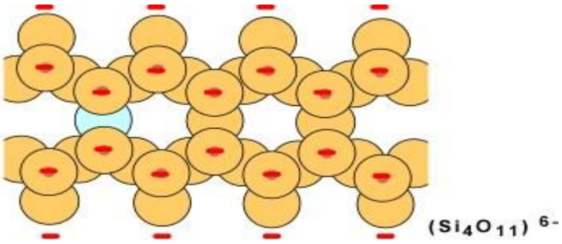
1.4.1.2.2. Monoclinic sodium pyroxenes

We distinguish jadeite $NaAlSi_2O_6$ and aegyrine $NaFeSi_2O_6$. However, the most widespread is aegyrine.

- **Aegyrine** It appears in elongated crystals, in acicular-shaped needles, sometimes striated or grooved.

1.4.2. Amphiboles ;

(Binding of double chains by metal ions), When two single chains unite



through their oxygens (in blue in the following diagram) to form double chains. The structural unit is therefore the ribbon (Si_4O_{11}) (OH) directed along the axis c . The general formula for **amphiboles** is as follows:

$W_{2x}(X,Y)_{7-2x}[(Si,Al)_4O_{11}(OH,F)]_2$

W = Ca, Na, K (gros cations)

X = Fe, Mg, Mn (moyens cations)

Y = Al, Fe, Ti (petits cations)

In the case of amphiboles, we still have the basic silicon-oxygen unit, but here a certain amount of oxygen atoms are replaced by hydroxyl radicals (not shown on the model). Unlike pyroxenes, we have double chains here. The positions available for iron and magnesium ions are at the periphery and at the top of the double chain (see above). The end view of a double chain shows the position occupied by iron and/or magnesium ions at the top and periphery. These ions unite several chains to form amphiboles.

As in the case of pyroxenes, there are planes of weakness which pass through the weakest links (red lines) and which define the cleavages. In this case, the planes are at 120° and the complement is 60°. Amphiboles therefore have two cleavage planes, one at 120° and the other at 60°.

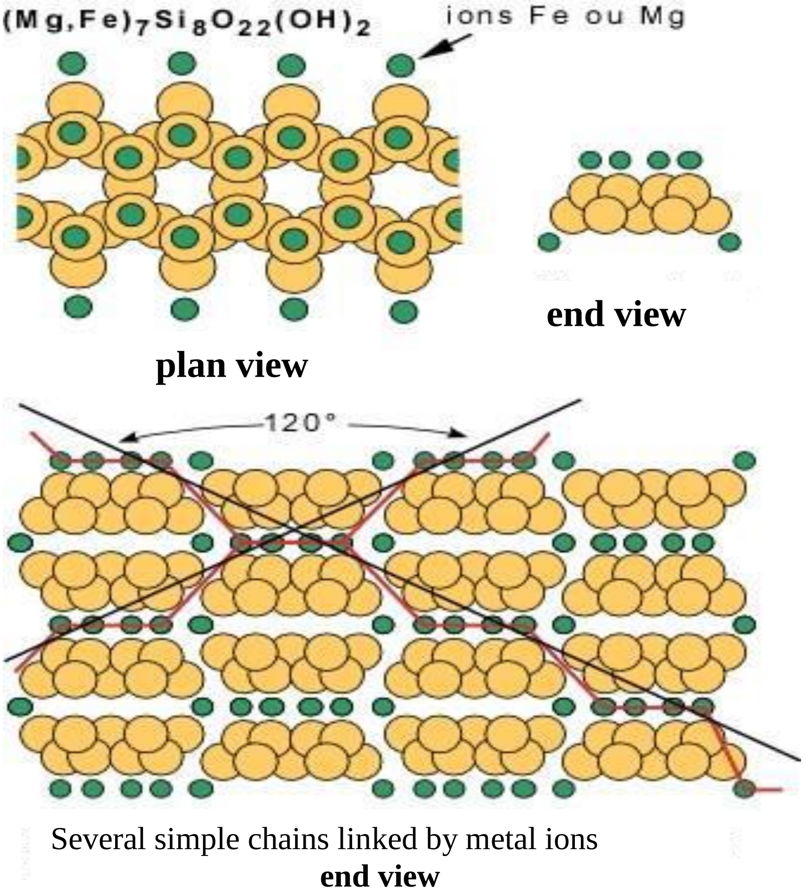


Figure 20. Amphiboles Structure two cleavage planes

Ex with 2 chains: Amphiboles (family of) Monoclinic

$Ca_2(Mg,Fe)_4Al(Si,Al)_4O_{11}(OH,F)_2$

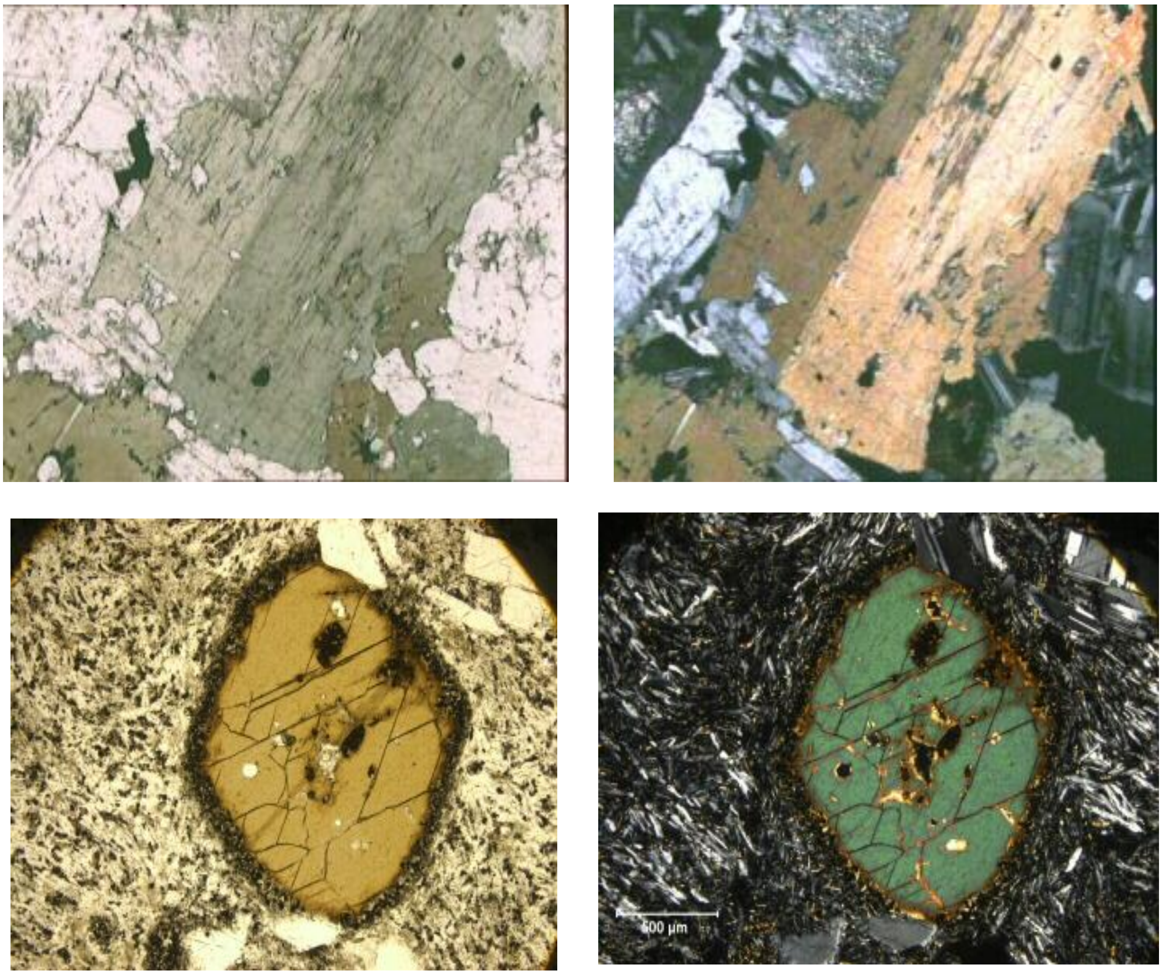


Figure 21 . Observation in LPNA and LPA of a "basic" Hornblende in a trachyte

1.4.2.1. Ferromagnesian amphiboles

They crystallize in the orthorhombic system because site X contains Fe, Mg. Among them we can distinguish anthophyllite with the formula: $[(Si_4O_{11})\ OH]_2\ (FeMg)_7$ Prismatic crystals are rare. It often occurs en masse compact, fibroradiate, fibrous. Color: gray, brownish, brownish green, to reddish brown.

Cleavage following the prism (110) with a cleavage of 120°. Glassy shine

Hardness=5.5 to 6 and density=2.8 to 3.2

Deposit: it is an essential mineral of crystalline shales.

1.4.2.2. Calcium monoclinic amphiboles

In this case site X contains Ca, the amphiboles belonging to this class are the actinolite-tremolite group and hornblende.

- **Actinote-tremolite :**It forms a solid solution since:

a magnesium term, tremolite: Ca_2 Mg_5 $[(Si_4O_{11})\ OH]_2$ towards a ferrous term, ferroactinote: Ca_2 Fe_5 $[(Si_4O_{11})\ OH]_2$, the intermediate term being *actinolite* of formula Ca_2 (Mg, Fe)$_5$ [(Si4O11) OH] $_2$, Crystals are rare in tremolite, however they are more common in actinolite; prisms more or less elongated, sometimes lamellar. Usually in acicular to fibrous aggregates.

White to dark gray color. Vitreous to silky shine; uneven breakage

Hardness = 5 to 6 and density = 2.9 to 3.2

Long-fiber asbestos is a fibrous variety of tremolite.

Deposit: tremolite is found mainly in crystalline limestones and dolomites. Actinolite in crystalline, chloritous or talcose schists.

- **Hornblende** Its formula is: $(Ca,Na,K)_{2\text{-}3}(Mg,Fe2+,Fe3+,Al)_5\ [(Si_3AlO_{11})\ OH]_2$ We distinguish green hornblende and brown hornblende or basaltic hornblende which is richer in iron.

Basaltic hornblende is generally well crystallized: elongated prismatic crystals with a hexagonal section. Green hornblende in loose, unclear crystals, in elongated flattened, fibrous, sometimes massive aggregates. Green Hb color: green, bluish green, light brown, blackish green.

Hb brown: brown to shiny black. Translucent. Subconchoidal breakage.

Hardness = 5 to 6 and density = 3 to 3.4

Alteration into epidote, serpentine, chlorite.

Deposit: brown Hb or basaltic Hb is more common in volcanic rocks (basalts, trachytes). Green Hb is found in granites, syenites, diorites, but also in rocks of contact metamorphism and in crystalline schists (amphibolites).

1.4.2.3. **Monoclinic sodium amphiboles**

Among the most important we will cite **riébekite** of formula: $[Si_4O_{11}\ (OH)]_2$ Na2 Fe3+4 . It occurs in irregular or fibrous prismatic crystals and in lamellar or asbestiform aggregates.

Color: blue black-to-black Glassy sheen but sometimes silky to shimmering

Perfect cleavage according to the vertical prism

Hardness = 5.5 to 6 and density = 3.02 to 3.42.

Deposit: riébekite is found in rocks of low temperature and low and medium pressure metamorphism, but also in alkaline magmatic rocks: in granites and syenites.

1.5. PHYLLOSILICATES:

Layered tetrahedra with intervention of Mg, Fe, K

- The sharing of 3 oxygens leads to a framework of infinite layers.
- The condensation of layers of pyroxenes or amphiboles gives a $[Si_4O_{10}]_4$ sheet – characteristics of micas, chlorites and clays.

When double chains join, each tetrahedron shares three oxygens (red in the diagram below) the general formula is Si_4O_{10} with a charge of – 4. We will have a layered structure.

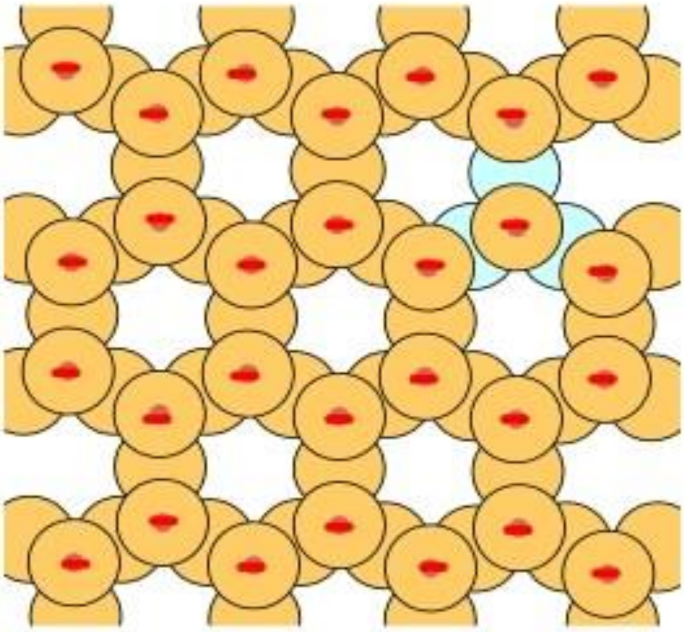


Figure 22. $[Si_4O_{10}]_4$ sheet in phyllosilicates

1.5.1. Architecture of phyllosilicates

The framework of phyllite minerals has a layered structure, formed by the **stacking** of tetrahedral layers (T) and octahedral layers (O). In **octahedral layer** ;

- Al ions occupying the center of Octahedra, the whole forms a layer of Octahedra: Octahedral layer of Gibsite $Al_2(OH)_6$ type. Called dioctahedral layer.

Or

- Mg ions occupying the center of Octahedra, the whole forms a layer of Octahedra: Octahedral layer of Brucite type: $Mg_3(OH)_6$. Called trioctahedral layer.

There are three types of possible patterns of association of these tetrahedral and octahedral layers, thus forming an elementary ***sheet***:

Table 6. Association of layers forming elementary ***sheet (minerals)***

Subgroup of the type	**Number of layers per sheet**	**Thickness of the sheet**	**Magnesian octahedral layer type minerals Brucite: Mg3(OH)6 trioctahedral**	**Aluminous octahedral layer type minerals Gibsite: Al2(OH)6 dioctahedral**
Kaolin	2	7.18	Antigorite $Mg_3(Si_2O_5)(OH)_4$	Kaolinite $Al_2(Si_2O_5)(OH)_4$
Talc /Mica	3	9.5 (talc)	Talc $Mg_3(Si_4O_{10})(OH)_2$	Pyrophylite $Al_2(Si_4O_{10})(OH)_2$
		10 (mica)	Phlogopite –Biotite $KMg_3(Si_3AlO_{10})(OH)_2$	Muscovite $K\ Al_2(Si_3AlO_{10})(OH)_2$
Chlorite	4	14	Chlorite $Mg_6(Si_3AlO_{10})(OH)_8$	

a. TO type structure (sheet 1/1)

The minerals of the **kaolin** family belong to this group, including kaolinite, dickite, nacrite, halloysite and dehydrated halloysite. The thickness of the kaolinite layer is 7Å with the absence of cations in the interfoliar space, while that of halloysite is 10 Å with an interfoliar space containing a layer of water molecules (Figure)

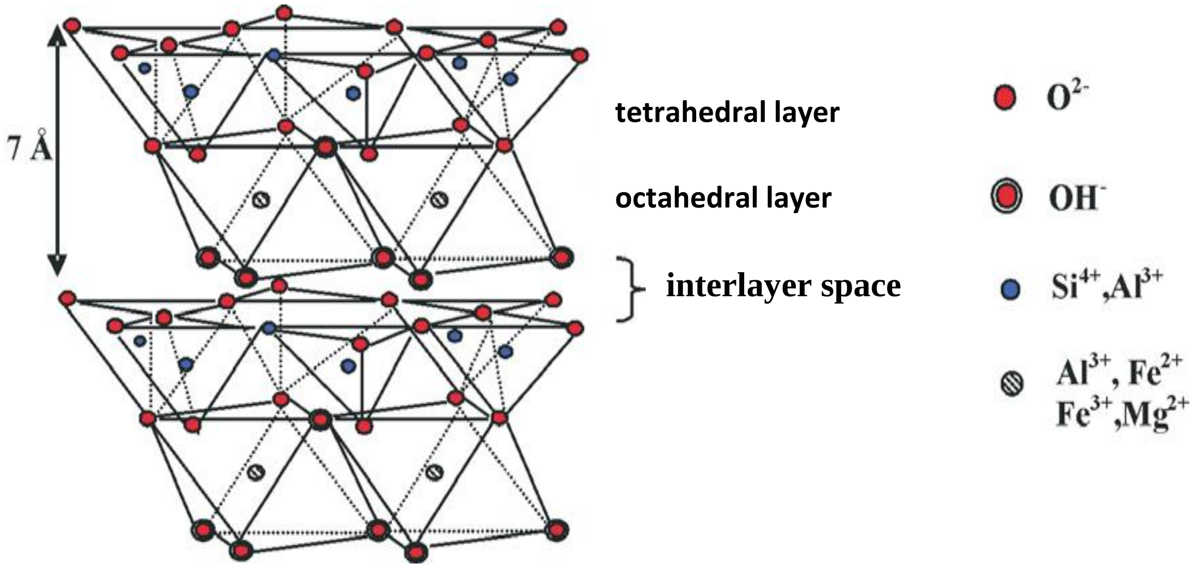


Figure 23 . Structure of TO type phyllite sheet

b. **TOT type structure (sheet 2/1)**

This structure corresponds to an octahedral layer sandwiched between two opposing tetrahedral layers. This family has two groups, one includes **micas, illite and glauconites** with a thickness of 10 Å, non-swelling with a constant inter-reticular

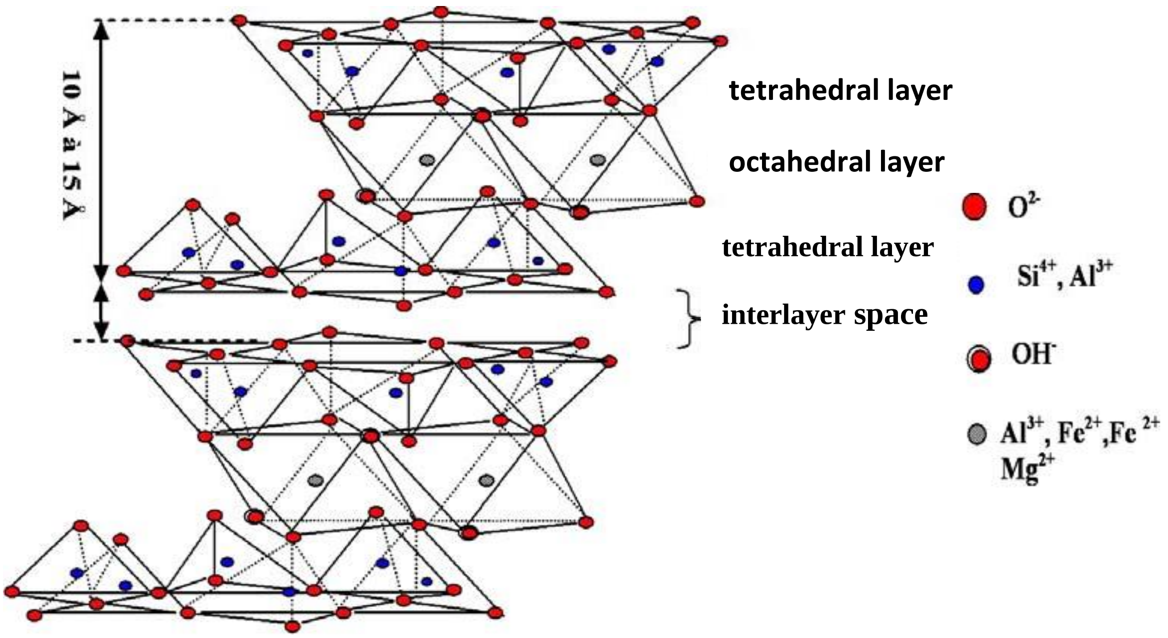


Figure 24 . Structure of a TOT type phyllite sheet

distance along the c axis; the other group includes **smectites** with variable interfoliar space and contain one or two layers of water molecules, these are swelling minerals. The thickness of their sheet is approximately 14 to 15 Å (Figure

c. TOTO type structure

In certain cases, the interfoliar space is occupied by a brucitic layer (Mg(OH)2) connecting elementary layers similar to those of micas: these are ***chlorites***, where the TOTO type structure. When the interfoliar space of the TOT continuous pattern is empty, pyrophyllite and talc can be distinguished. But, when the TOT pattern is discontinuous and the interfoliar space contains zeolite water, the **clay is called fibrous**. These are pseudo-sheets of sepiolite and palygorskite (Brindley and Brown., 1980; Caillère et al., 1982).

The classification of TOT type minerals is based on the value of the interfoliar charge x, the nature of the substitutions and the degree of occupation of the octahedral layers. According to certain authors (Caillère et al., 1982), to make a classification of 2:1 type minerals, it is necessary to start from minerals having a zero charge, considered as parents. These are talc (trioctahedral mineral) and pyrophyllite (dioctahedral mineral) from which the 2:1 minerals derive, and this by isomorphic substitutions. These substitutions can be:

- Tetrahedral, with Si often substituted by Al or Fe,
- octahedral with Al3+ substituted by Fe3+, Fe2+ or Mg2+ in dioctahedral species and Mg2+ substituted by Fe3+, Fe2+ or Al3+ in trioctahedral species (Brindley and Brown, 1980).
- Interfoliar with K, Na, Ca substitutions, known in micas.

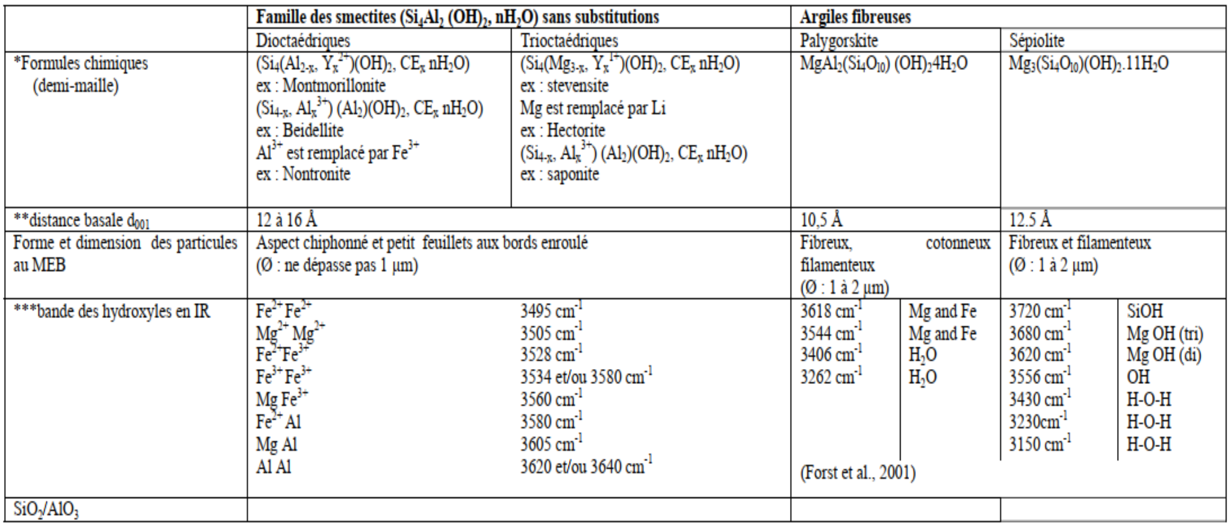
In nature, fully charged substitutions (1,2) occur particularly in micas. Let us cite, for example: muscovite (potassium dioctahedral mineral with interfoliar charge equal to 1) and clintonite (calcic trioctahedral mineral with interfoliar charge equal to 2). Most often, substitutions can simultaneously involve tetrahedra and octahedrons, particularly in smectites where the compensating cations can be (Mg, Ca, Na, K) (Brindley and Brown, 1980), and the charge value is less than 1.

Phyllosilicates can be subdivided into two groups, according to the occupation of octahedral sites:

¾ The dioctahedral series, where two octahedral cavities out of three are occupied. The third is vacant, for example muscovite and illite. In kaolins, the large vacant site is surrounded by six smaller occupied octahedra (Brindley and Brown., 1980).

¾ The trioctahedral series, where the three octahedral sites are occupied, for example talc. The determination of the di- or tri-octahedral character is carried out by the infrared study of OH valence vibrations. Thus, for dioctahedral minerals the OH dipole is directed towards the vacant site and will be inclined by 20 degrees relative to the plane of the sheet. He generates a band called “vacancy band = band V”. In trioctahedral species, the OH dipole is normal to the plane of the sheet and generates a band called “Normal band = N band”. These nomenclatures are those of Vedder (1964).

Table 7. Characteristics of minerals belonging to smictites and fibrous minerals (palygorskite et sépiolite)



	Famille des smectites ($Si_4Al_2(OH)_2, nH_2O$) sans substitutions		**Argiles fibreuses**	
	Dioctaédriques	Trioctaédriques	Palygorskite	Sépiolite
*Formules chimiques (demi-maille)	$(Si_4(Al_{2-x}, Y_x^{2+})(OH)_2, CE_x\, nH_2O)$ ex : Montmorillonite $(Si_{4-x}, Al_x^{3+})(Al_2)(OH)_2, CE_x\, nH_2O)$ ex : Beidellite Al^{3+} est remplacé par Fe^{3+} ex : Nontronite	$(Si_4(Mg_{3-x}, Y_x^{1+})(OH)_2, CE_x\, nH_2O)$ ex : stevensite Mg est remplacé par Li ex : Hectorite $(Si_{4-x}, Al_x^{3+})(Al_2)(OH)_2, CE_x\, nH_2O)$ ex : saponite	$MgAl_2(Si_4O_{10})(OH)_24H_2O$	$Mg_3(Si_4O_{10})(OH)_2.11H_2O$
**distance basale d_{001}	12 à 16 Å		10,5 Å	12.5 Å
Forme et dimension des particules au MEB	Aspect chiphonné et petit feuillets aux bords enroulé (Ø : ne dépasse pas 1 µm)		Fibreux, cotonneux filamenteux (Ø : 1 à 2 µm)	Fibreux et filamenteux (Ø : 1 à 2 µm)
***bande des hydroxyles en IR	$Fe^{2+}Fe^{2+}$ $Mg^{2+}Mg^{2+}$ $Fe^{2+}Fe^{3+}$ $Fe^{3+}Fe^{3+}$ $Mg\,Fe^{3+}$ $Fe^{2+}Al$ Mg Al Al Al	3495 cm^{-1} 3505 cm^{-1} 3528 cm^{-1} 3534 et/ou 3580 cm^{-1} 3560 cm^{-1} 3580 cm^{-1} 3605 cm^{-1} 3620 et/ou 3640 cm^{-1}	3618 cm^{-1} Mg and Fe 3544 cm^{-1} Mg and Fe 3406 cm^{-1} H_2O 3262 cm^{-1} H_2O (Forst et al., 2001)	3720 cm^{-1} SiOH 3680 cm^{-1} Mg OH (tri) 3620 cm^{-1} Mg OH (di) 3556 cm^{-1} OH 3430 cm^{-1} H-O-H 3230cm^{-1} H-O-H 3150 cm^{-1} H-O-H
SiO_2/AlO_3				

Micas. In the case of micas, whose base-structure is formed by planar layers of tetrahedra, the available positions for iron and magnesium ions are at the top of the layer (see above), as shown in the end view. a diaper. In micas there are two types of planar layers: the tetrahedral layer, denoted T and formed of silicon-oxygen tetrahedra (a certain quantity of aluminum can substitute for silicon), and the octahedral layer, denoted O and formed of ions Fe-Mg and oxygens. These two types of layers form sheets, which are united by large ions, such as potassium in the case of muscovite, a common mica. Micas have a cleavage plane, parallel to the layers.

Group of micas: biotite, muscovite, glauconium, phlogopite, lepidolite etc,….

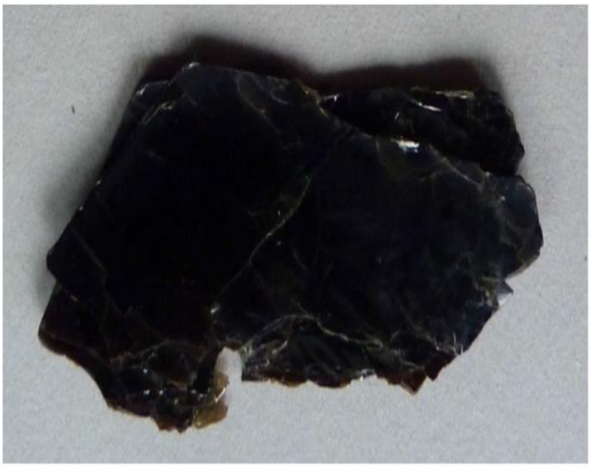


Figure 25a. Photo of biotite

Figure 25b. Photo of muscovite

Monoclinic Biotite $K(Mg, Fe)_3\ AlSi_3O_{10}\ (OH, F)_2$

Muscovite Monoclinic $K\ Al_2\ Si_4O_{10}\ (OH, F)_2$

Monoclinic Glauconite $(K, Na, Al)_2\ (Fe, Al, Mg)_4\ [Si_6O_{20}]\ (OH)_4$

Clay group : Triclinic Kaolinite $[Al_2Si_2O_3\ (OH)_2]$

Smectite Montmorillonite (fam.) Monoclinic $(Al, Mg)_2\ Si_4O_{10}\ (OH)_2\ Na(H_2O)_4$

Talc Monoclinic $Mg_3\ (Si_4O_{10})\ (OH)_2$

Chlorite (family) Monoclinic $(Mg,Fe,Al)_3Mg_3\ (Si,Al)_4O_{10}\ (OH)_8$

Serpentines (family of) Monoclinic or Orthorhombic $Mg_6\ [Si_4O_{10}\ (OH)_2]\ (OH)_6$

Recognition of phyllosilicates : « Biotite »

Note the frequent presence of alterations in the biotite. This alteration is green in

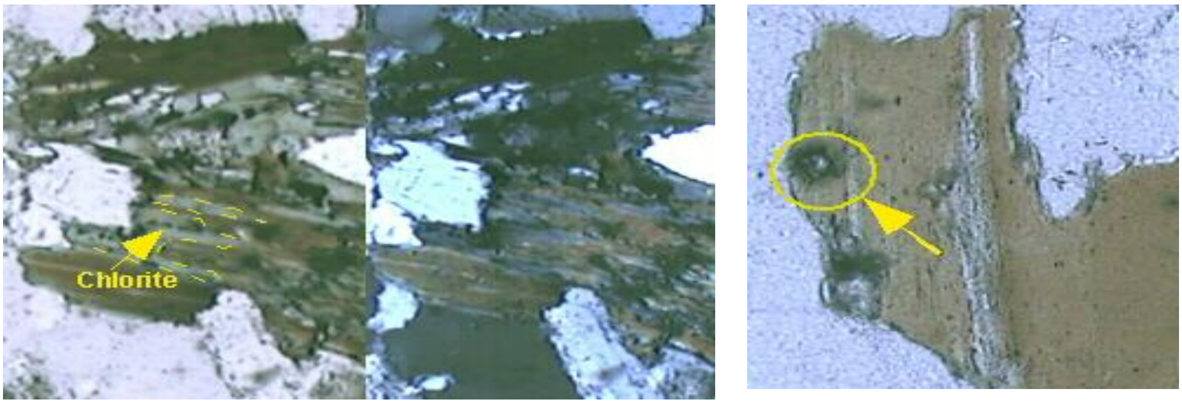


Figure 26. Chloritization of biotite. Note the abnormal hues of the Pleochroic halo" in biotite (metamictization chlorite (l.: LPNA; dr. LPA)")

LPNA and takes on abnormal hues in LPA (midnight blue, brown). This is a transformation into chlorite (see photo). We also note the presence of black spots in LPNA, sometimes around inclusion crystals in biotite, with strong relief and very strong birefringence hues. This is an amorphization of the mineral (metamictization) due to the accumulation of irradiation damage caused by the radioactive elements of the included mineral, often zircon.

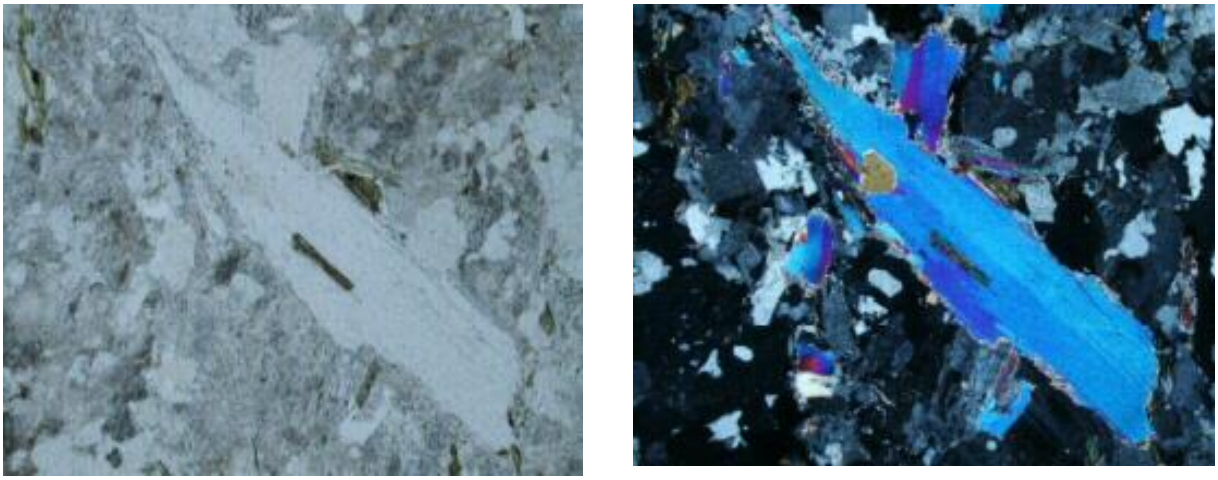


Figure 27. Muscovite (g. : LPNA; dr. LPA)

1.6. TECTOSILICATES

- Very important family in Earth sciences because the minerals which constitute it are the major constituents of the continental crust, therefore defining families of rocks, among these minerals quartz, and feldspars,…

In the case of quartz, there are no metal ions since their oxygens to form a three-dimensional network

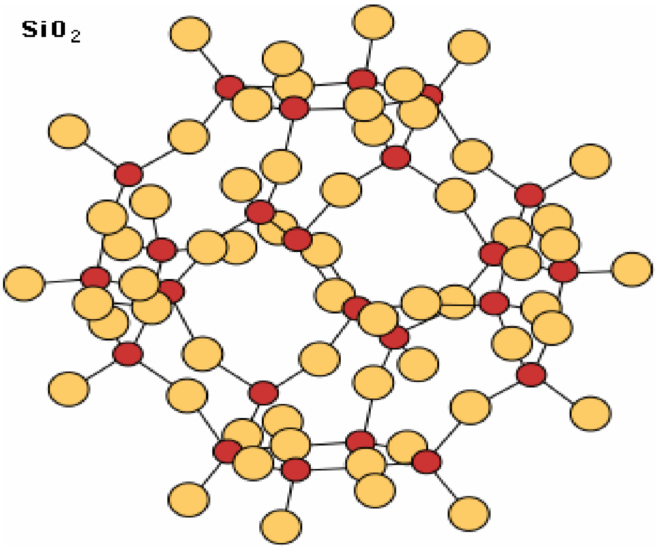


Figure 28. Three-dimensional network of SiO_2

link all the corners of the tetrahedra together. There are no plans of weakness, therefore no cleavage.

In feldspars, the structure is more complex. Tetrahedra are of two types: SiO_4 tetrahedra and AlO_4 tetrahedra. These form a three-dimensional network where the corners of the tetrahedra are linked by the oxygens, with positive ions Na, K, Ca located in the interstices of the negatively charged network.

Tectosilicates are silicates whose arrangement of tetrahedra consists of a three-dimensional framework where each oxygen of the vertices of the tetrahedra is shared with neighboring tetrahedra. The typical model is quartz [SiO_2]. (SiO_4 tetrahedra all have their vertices in common.)

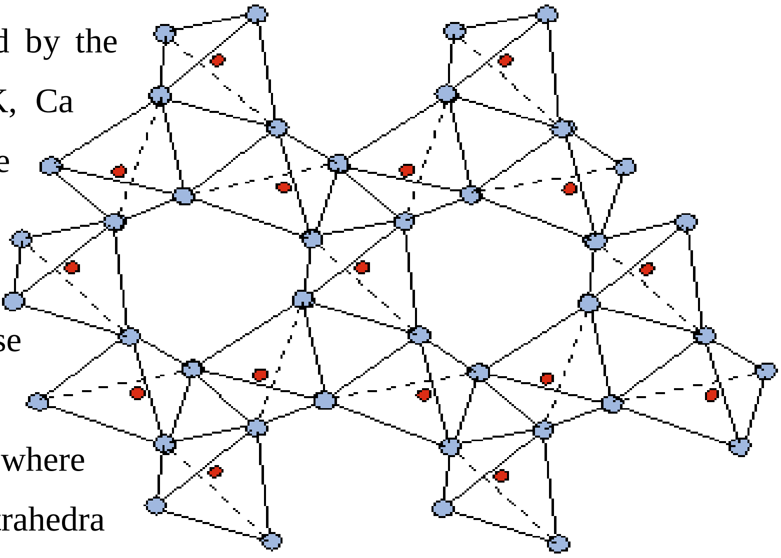


Figure 29. 3D view of the architecture of tectosilicate.

1.6.1. SiO_2 Group

a. **Quartz** (SiO_2) : It crystallizes in the pseudo-hexagonal rhombohedral system, it often has a bi-pyramid shape.Color: although normally colorless (rock crystal or hyaline quartz), quartz can present numerous colors (allochromatism phenomenon). We thus distinguish:

Rose quartz, color due to traces of Mn or hematite inclusions. Yellow quartz or citrine color due to traces of colloidal ferric hydroxides. Purple quartz or amethyst color due to traces of Re3+.Black or smoky quartz Milky white quartz. In these last 2 cases the coloring would be linked to a particular electronic distribution. Tiger's Eye: variety of silica with shimmering reflections.

Hardness: 7

Conchoidal breakage, greasy to vitreous shine.

No cleavage, but presence of twins through penetration or bonding.

Deposit: It can be present in all types of rocks, whether magmatic, metamorphic or sedimentary.

In igneous rocks, it is involved in the classification of rocks as a cardinal mineral in the same way as feldspars and feldspathoids. It characterizes supersaturated rocks. It is found in granites, granodiorites, quartz diorites and their effusive equivalents. In metamorphic rock, it is present both in rocks of contact metamorphism and in those of general metamorphism.

In sedimentary rock, it characterizes sandstones.

b. **Chalcedony and opal** (SiO_2) n H_2O These are products of concretion of silica in a sedimentary context (flint, chert) or igneous (agate nodules, filling of vacuoles) . Chalcedony can be subdivided into chalcedony in the strict sense with uniform coloring, and agate variously colored in parallel or concentric bands. They can be white, red, brown or green. Opals are called hyalite when they are colorless and transparent with a bold sheen, and noble opal when they are translucent but reflective of light.

c. **Tridymite and cristobalite** : Tridymitis is found in 2 forms:

-high temperature, crystallizing in the hexagonal system

-low temperature crystallizing in the orthorhombic system

It generally comes in thin twinned hexagonal plates 2 by 2 or 3 by 3.

It also comes in rosettes of white crystals.

Deposit: tridymite is a mineral from acidic volcanic rocks: trachytes, andesites and rhyolitic tuffs.

Cristobalite is also found in

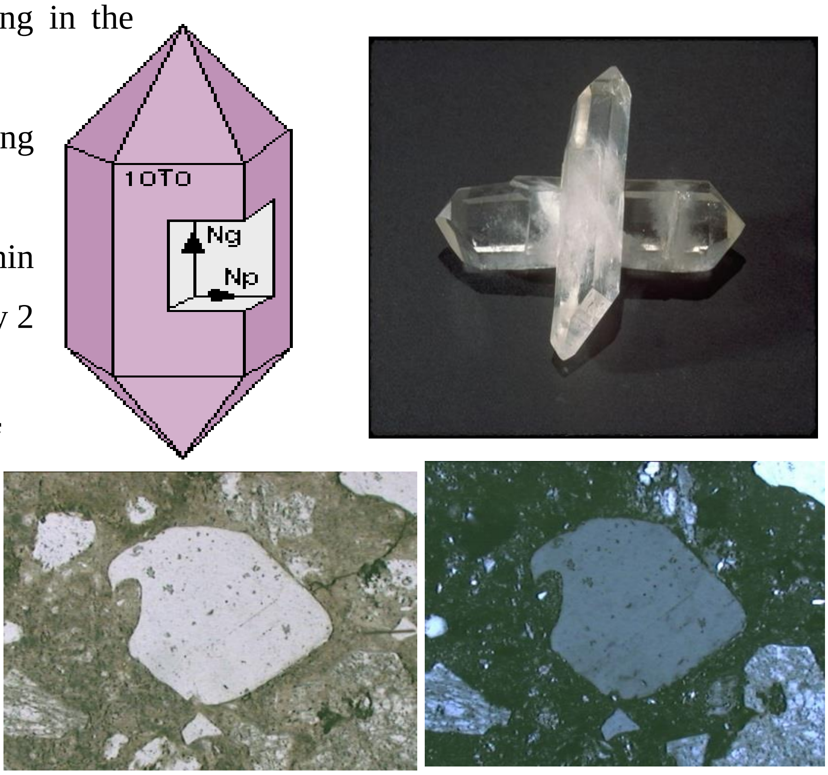


Figure 30. a.Quartz crystallizing in the rhombohedral system.
b.Automorphic quartz in a rhyolite (LPNA) and (LPA)

2 forms:

- High temperature, crystallizing in the cubic system .It appears in the form of octahedral crystals, sometimes twinned on
- Low temperature crystallizing in the quadratic system

(111), or in spherolitic masses.

Deposit: it is associated with tridymite.

1.6.2. PLAGIOCLASE- FELDSPARS

Feldspars are the most common minerals in the earth's crust. Their redominance makes it possible to define the classification of igneous rock.

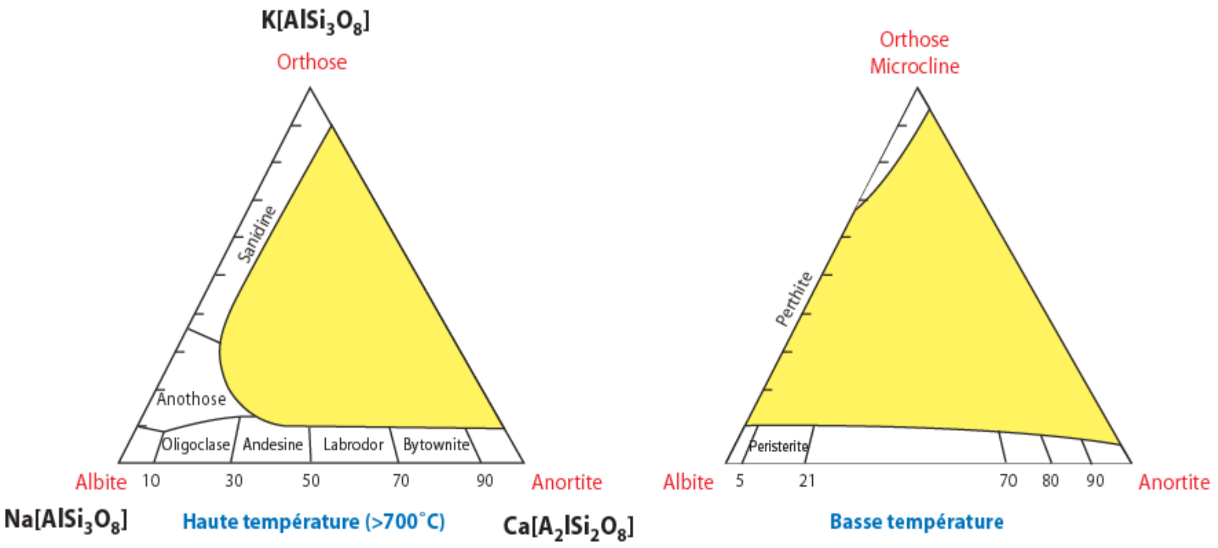


Figure 31. Diagram of Plagioclase and Feldspars

The term solid solution reflects the possibility that there exists an expression of the exchange between two or three pure poles. It induces the development of diagrams according to P, T and the composition (X, P, T).

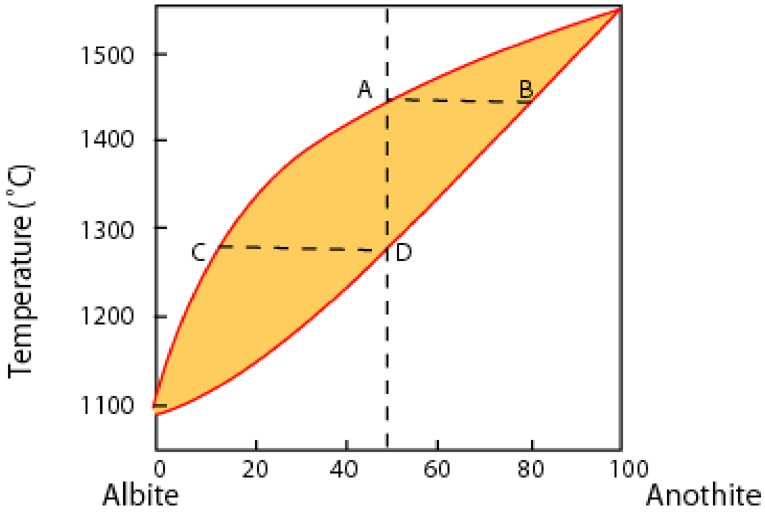


Figure 32. Plagioclase ; solid solution between two chemical poles.

Feldspars are built on the same model. However, Si-Al substitutions can occur. Indeed, when the ions have a relatively similar ionic radius, the ions can substitute each other, Al3+ is therefore incorporated into the tetrahedral sites in substitution for Si4+. Note that the substitution does not necessarily imply that the ions are of the same charge.

1. multiply the formula [SiO_2] by 4 -> [Si_4O_8].

2. we then substitute a Si^{4+} with an Al^{3+} -> [Si_3AlO_8]$^-$ (a negative charge appears). the electric charge is compensated by a monovalent cation K+: potassium feldspar [Si_3AlO_8]K or Na+: albite [Si_3AlO_8]Na

3. we substitute two Si^{4+} by two Al^{3+} -> [$Si_2Al_2O_8$]$^{2-}$ (two negative charges appear)

the electric charge is compensated by a bivalent cation Ca^{2+}: anorthite [$Si_2Al_2O_8$]Ca

The Na^+ and Ca^{2+} ions have neighboring ionic radii; they can then substitute each other. We call a solid solution a series of minerals whose formula evolves between two extreme poles; we also speak of an isomorphic series. The series between albite and anorthite is called the plagioclase series; its general formula is: (Na,Ca)[$Si_2Al(Si,Al)O_8$]

Another way to write it is to determine precisely the amount of silicon and aluminum in the plagioclase. Let us call ^{2} the mole fraction of silicon which remains after substitution by aluminum in plagioclase. The formula can be written: **[$Si_{2+x}Al_{2x}O_8$](Na_x,Ca_{1-x})**

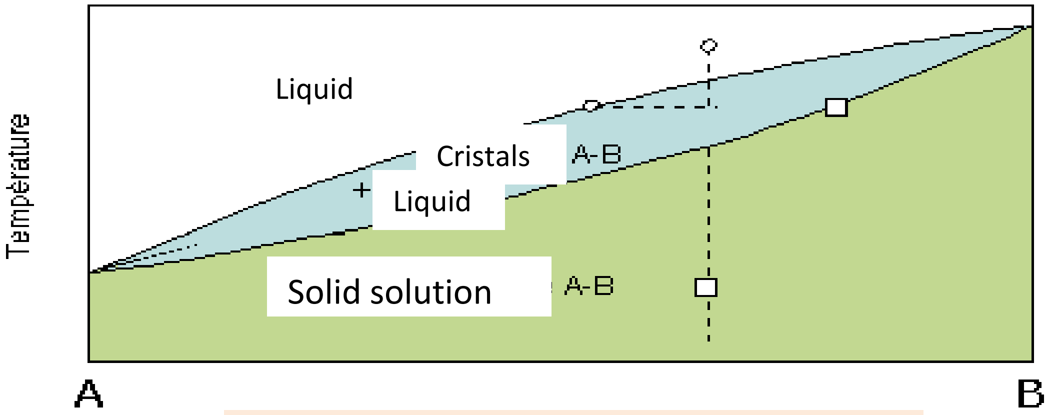


Figure 33. Binary system with solid solution (*Albite-anorthite phase diagram).*

The mole fraction of albite in plagioclase can be determined using powerful methods, such as the microprobe, which we will talk about again, or simpler optical methods (Michel-Levy method). The formula we have just written is a structural formula, that is to say it includes information on the structure (notation in square brackets) and the composition, that is to say the mole fraction of each element in the mineral. The structural formula of a mineral depends on many factors, including the availability of elements in the magma that is crystallizing and the competition between the different mineral phases being crystallized.

Recognition of plagioclase under the microscope

The most easily recognizable criterion for the identification of plagioclase under the microscope is the existence of polysynthetic twins, called "pajamas".

Figure 34. Plagioclase: polysynthetic twins (LPA)

1.6.3. ALKALINE FELDSPARS

Feldspars with Na and K are called alkali feldspars. There is a solid solution between albite and orthoclase stable only under certain conditions (high pressure and high temperature). Several cases arise:

Figure 35. Orthoclase cristal

• the rock crystallizes in conditions of great depth (high pressure): the albite and orthoclase then crystallize independently, there is no passage through the single feldspar stage.

• the rock crystallizes at shallow depth (low pressure): there is a single alkali feldspar

- The rock slowly rises to the surface: the two minerals can no longer coexist in the same structure, there is then exsolution

- The rock rises quickly, exsolution cannot occur, a single alkali feldspar then persists in the rock (Na and K at the same time)

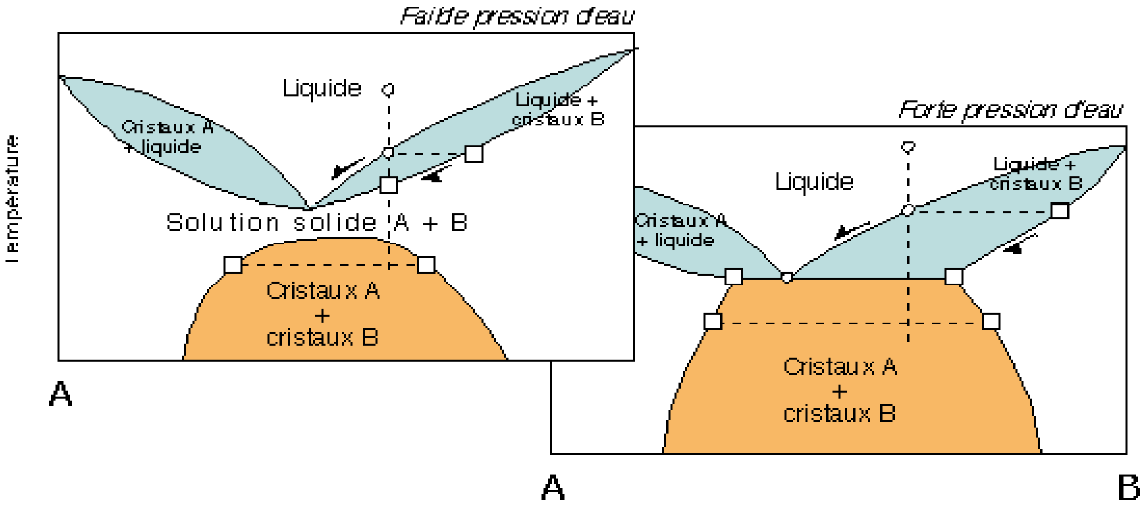


Figure 36. Albite –orthoclase phase diagram

The different varieties of alkali feldspars

The different forms of alkali feldspars depend on the conditions of formation and the extent of solid solutions. In low pressure and high temperature varieties, there is a complete solid solution between albite and orthoclase. Two cases arise depending on the cooling conditions: in the case of slow cooling, the exsolution phenomenon occurs.

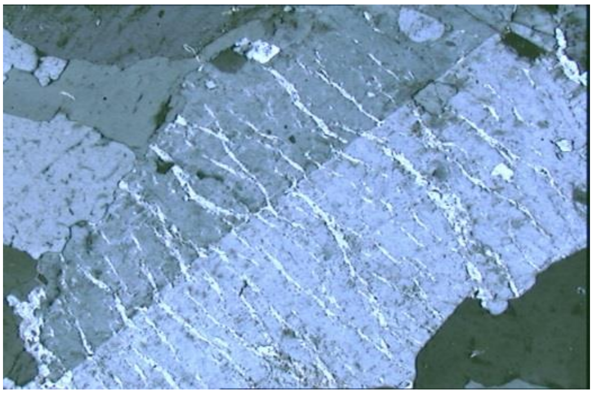


Figure 37. Perthite: exsolution of albite in a microcline

Orthoclase Monoclinic K Al Si_3O_8

Albite Triclinic Na Al Si_3O_8

Anorthite Triclinic Ca Al Si_3O_8

General characteristics of feldspars

Feldspars have a large number of common characteristics, whatever the species to which they belong. When they are not altered, they are porcelain white or more rarely colorless. They crystallize in monoclinic or triclinic systems.

Perfect (001) and imperfect (010) cleavages are common to all feldspars.

Feldspars are very often twinned: Carlsbad twin: simple, adjoining of 2 individuals is characteristic of potassium feldspars (orthoclase and sanidine).

Albite twin: polysynthetic by the joining of several individuals characteristic of plagioclase.

Pericline twin: this is a polysynthetic twin of albite and

Microcline. The grid observed in LM of the microcline corresponds to the combination of albite and pericline twins. Feldspars are often automorphic. Feldspars are generally translucent and rarely transparent.

Color: Feldspars are milky white, grayish or pinkish (orthoclase) or light green, notably microcline that called amazonite. The luster of feldspars is glassy and sometimes pearly to iridescent.

Their hardness is 6 and their density is between 2.5 and 2.7.

Deposit: Feldspars are the cardinal minerals of igneous, supersaturated, saturated and even undersaturated silica, grained, micrograined or microlitic rocks.

Alkal6i feldspars are more common in acidic rocks and potassic pegmatites while plagi+oclase are more abundant in basic rocks (diorites, gabbros).

In metamorphic rocks, microcline is the main representative of feldspars. In detrital sedimentary rocks, orthoclase feldspars appear in feldspathic or arkose sandstones.

Alteration of feldspars: Potassium feldspars alter into kaolinite by leaching of alkalis, or into damourite, sericite or saussurite (epidote by hydration of basic plagioclase).

1.6.4. FELDSPATHOIDS

Néphéline Hexagonal $Na_3K (SiAlO_4)$

Leucite Quadratic $K (SiAlO_6)$

Sodalite Cubic (Na8Cl2) (SiAlO4)6

Noséane Cubic (Na2SO4) (SiAlO4)6

Haüyne Cubic (Na, Ca)8-4 (SO4)1-2 (SiAlO4)6

Feldspathoids are tectosilicates. The Si-Al substitution is more important. On the other hand, these minerals are not stable in the presence of quartz; they react with the siliceous magmatic liquid to form feldspars (peritectic reaction).

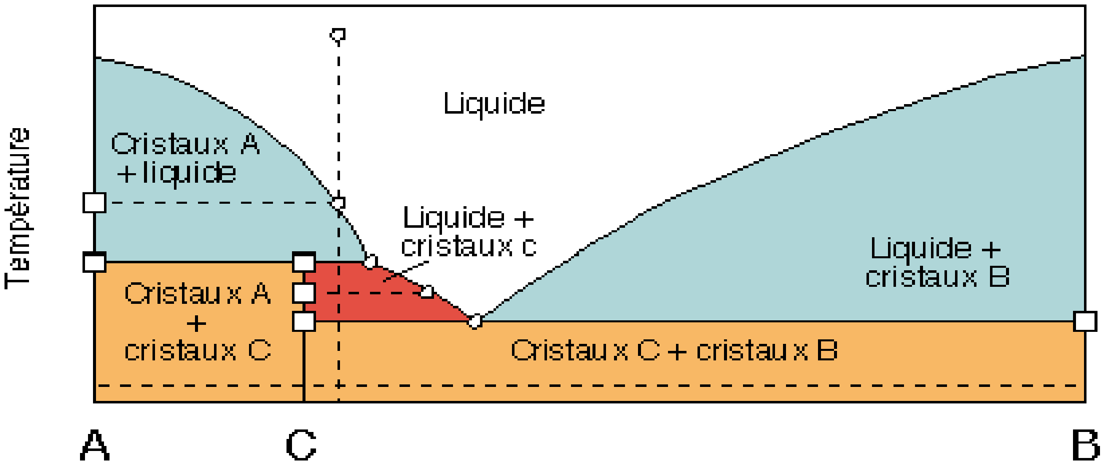


Figure 38. *Leucite-quartz phase diagram*

The magma in which these minerals precipitate is poor in silica; we speak of undersaturated magma. Fedspathoids are therefore minerals that indicate a lack of silica in the initial magma. The main feldspathoids are:

- leucite $[Si_2AlO_6]K$
- nepheline $[SiAlO_4]_4Na_3Al$
- the haüyne-sodalite-noséane isomorphic series

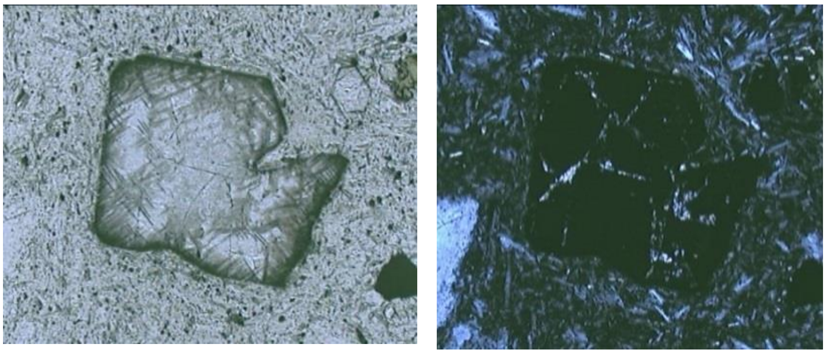


Figure 39. *Haüyne (feldspathoid) in (LN) and (LPA)*

Mutual relationships between tectosilicates (*quartz-albite).*

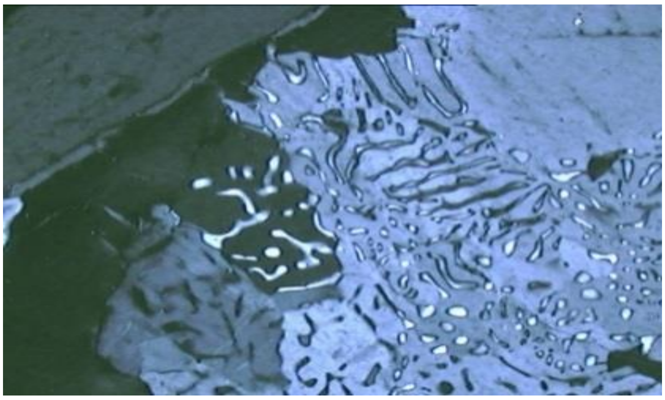


Figure 40. *Mymekite: quartz-albite interpenetration (LPA)*

1.6.5.Zeolite group (46 species): ***:***

They are tecto-silicates characterized by large channels that contain loosely bound water molecules (zeolite water). This water can be absorbed or resorbed reversibly, in response to variations in partial pressure of water vapor or heating (At moderate temperature, the silicate skeleton remains rigid. The expelled zeolite water can be reversibly replaced by different gaseous atoms or molecules ($H2S$, $NH3$,$CCl4$, Ar, Xe, Ne, etc.) or metals (Hg), hence their use as molecular traps in vacuum pumps, and as selective traps of small molecules in a mixture (molecular sieve).

These are hydrated alumino-silicates whose negative charges of the framework are compensated by Ca, Na, and K and more rarely by Ba, Sr, and Mg. The chemical formulas of zeolites correspond to the relationship:

$(CaO + Na2O + K2O + BaO + SiO + MgO) / Al2O3 = 1$

These cations which are also housed in the channels are poorly bonded, they are easily exchangeable between them 2Na Ca hence their use in the softening of hard water.

According to their structure and their facies, we distinguish 3 families:

* **Fibrous zeolites**: elongated facies, acicular to fibrous, they form fibroradiated groups.

- Natrolite: Na_2 $(Al_2Si_3O_{10})$ 2 H_2O, which crystallizes in the system orthorhombic.

- Mesolite: Na5Ca2 (Al2Si3O10) 8H2O which crystallizes in the system monoclinic.

*** Lamellar zeolites**: flattened facies, easy cleavage according to 010.

- Heulandite: $(Ca,Na)_2$ $(Al_2Si_7O_{18})$ 6 H_2O, crystallizes in the system monoclinic.

- Stilbite: (Ca, Na2, K2) (Al2Si7O18) 7H2O, crystallizes in the system monoclinic.

2. **Isometric zeolites**: they are excellent molecular sieves; their symmetry is pseudo cubic or cubic.

- Chabazite: (Ca, Na2) $(Al_2Si_4O_{12})$ 6 H_2O crystallizes in the system rhombohedral.

- Pargasite: (Ca, Na2) (Al_2Si4O_{12}) 16 H2O crystallizes in the cubic system.

Zeolites are colorless or white with yellowish, greenish or reddish reflections. Vitreous to silky shine.

Hardness between 4 and 5.5, density 2 to 2.5 Zeolites can be distinguished from each other by an X-ray study

Deposit: They are generally present in association with calcite in the vacuoles of effusive rocks (basalts) and in pegmatites.

II.2. NON-SILICATED MINERAL SPECIES.

If the rocks constituting the earth's crust are generally made of more than 95% silicates, the remaining few % are made of so-called “accessory” minerals, the study of which is sometimes important to explain the petrogenesis of the rock. These minerals are sometimes of very strong economic interest (precious metals, strategic minerals, diamonds, etc.). Furthermore, if among igneous or plutonic rocks exclusively silicate varieties constitute the overwhelming majority, it is not the same among sedimentary and metamorphic rocks where carbonate rocks are important, not to mention evaporites, bauxites, phosphate deposits, etc. This is why it is unjustified to ignore non-silicate mineral species classified as:

- Native elements (metals, semi-metals and metalloids)
- Oxides and hydroxides
- Sulphides
- Sulfates
- Carbonates
- Phosphates
- Halides.

Without forgetting nitrates and borates as well as chromates, molybdates and tungstates as well as the much rarer arsenates and vanadates.

2.1. The Native Elements:

The term “native” refers to a chemical element, often metallic, which is found in nature in its pure state. There are approximately 80 native elements or alloys. Native elements are quite rare but have great economic importance. We distinguish between native metals (gold, silver, copper), semi-metals (Bi, Sb, As, Te, etc.) and metalloids (carbon, sulfur).

2.1.1. Native metals:

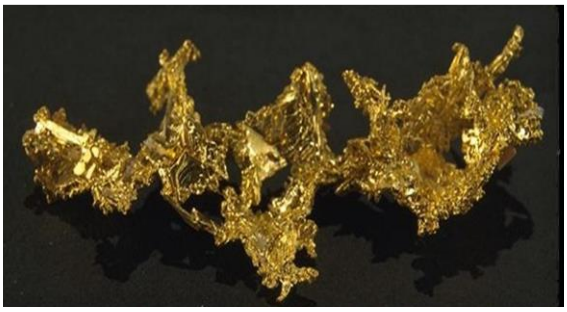


Figure 41. Gold in form of nuggets

Copper, silver, gold, platinum, nickel and exceptionally chromium and iron are sometimes present in their native state. They very rarely appear in the form of crystals but rather in the form of chips, sheets, threads, dendrites and sometimes nuggets. Their hardness varies from 2 to 5 and their density, high, from 8 (Fe) to 21 (Pt). They have a strong metallic luster but no cleavage and are malleable. They are also good conductors of current.

2.1.2. Native semi-metals:

Bismuth, antimony, arsenic, tellurium are semi-metals. Their luster is variable (metallic to submetallic) and their density is high. They are more or less malleable and have cleavages.

2.1.3. Native metalloids:

Metalloids (carbon, sulfur) are fragile (except, of course, C diamond), not very dense and have many forms, such as carbon, whose best-known polymorphs are graphite and diamond.

Graphite: Graphite is composed of carbon atoms arranged in hexagonal rings. This hexagonal structure also has a layered character. It forms in certain sedimentary rocks undergoing metamorphism (high pressure and temperature): graphite schists for example. It can be formed from vegetable charcoal. The uses of graphite are numerous: - Pencil - Batteries (electrode) - Sports articles (tennis rackets, ski sole, etc.) - Adsorbent (carbon filters) - Constituent of mechanical parts (friction parts, ...) - Constituent of Lubricants - Electrical connections in motors (electricity transfers to the rotor) = motor brushes (= washing machine motor carbon, etc.)

Diamond: Like graphite, diamonds are made of carbon. The difference is that they form under extreme temperature and pressure conditions: between 1100°C and 1400°C for temperature, and for pressure, between 4.5GPa and 6GPa, which corresponds to depths of around 150 to 1000 km in the terrestrial mantle. The origin is therefore magmatic and its formation conditions explain its very high hardness (The hardness of diamond is 10/10 on the Mohs scale). This property is the source of many current uses: cut organs. The structure of the diamond is cubic, its thermal conductivity is exceptional, and would help revolutionize electronics in the future, limiting heating and therefore electricity consumption.

Natural diamond mines are found, for example, in South Africa in eruptive rocks called “kimberlite pipes (name of the rock)”. The main natural diamond producing countries are: Russia (1st in the world with 20% of world production), Congo, Botswana, Central African Republic, Australia, South Africa (10%). Nowadays production of artificial diamonds is in booming could one day supplant production through extraction. Resistant to high temperatures (1,000°C), high powers and capable of responding to high frequencies, artificial diamond on paper supplants silicon, the semiconductor material with which 90% of electronic components are still made today. 'today. However, the latter easily shows its weaknesses, because its temperature limit for use is around 200°C. A significant handicap for applications in extreme conditions, in aeronautics, space or nuclear power, where very resistant transistors are required. In theory therefore, of all semiconductors, diamond is the best, the fastest, the most resistant. It remains to resolve the problem of the production cost of artificial diamond and to master its semiconductor properties.

Sulfur (S): Sulfur can have a volcanic origin by condensation of magmatic gases containing hydrogen sulfide (H_2S) - toxic gas. But most of the time, it has a sedimentary origin (for example following the reaction of reduction of sulfates (gypsum) by the carbon of organic matter). 90% of sulfur is used to prepare sulfuric acid, a basic product of the chemical industry (treatment of ores and metals, synthesis of household detergents, batteries, etc.). It is used in particular as a fertilizer (sulphates) (60% of production) and a phytosanitary fungicide (against powdery mildew in vines). It is also used to make gunpowder, laxatives (magnesium sulfate), matches, insecticides, etc. Sulfur dioxide (SO_2 from the combustion of sulfur) is an antioxidant and acid used to stabilize wine. Sulphites (from the reaction between sulfur dioxide and water) are used to whiten paper. Desulfited are added to foods to prevent browning or discoloration. These are preservatives (food, medicines) and antimicrobial agents. This element also found in small amounts in coal and oil, which produce sulfur dioxide when burned. Fuel standards increasingly require that sulfur be extracted from fossil fuels, because sulfur dioxide combines with water in the atmosphere (rain droplets) to produce acid rain, which causes forest dieback.

2.2. Oxides And Hydroxides:

There are approximately 320 oxides and hydroxides. Compounds of metals or metalloids with oxygen or hydroxide groups have sometimes been grouped somewhat arbitrarily, sometimes with replacements by fluorine or chlorine. By tradition, we include “multiple oxides” which, from a purely chemical point of view, should be considered as salts: spinels, tantalites, niobates, certain titanates and some antimoniates and uranates.

Although simple oxides and “multiple oxides” have very variable properties, we can nevertheless notice certain convergences between the most important of them: hardness sometimes 8 (spinel, gahnite, etc.) or more (corundum, nigerite, chrysoberyl, …) and **great chemical stability**, hence low solubility and a high melting point, and they also often exhibit good cleavage. On the other hand, hydroxides often have low hardness, unlike harder oxides.

We find a very great diversity in the conditions of deposits of these minerals. Most single oxides and “multiple oxides” belong to the domains of magmatism, metamorphism and marine sedimentation. The majority of hydroxides are found in the oxidation zone of metal deposits and, more generally, in the rock alteration zone.

2.2.1. Oxides:

_ Rhombohedral Corundum Al_2O_3;

_ Rhombohedral Hematite Fe_2O3;

_ Hexagonal Ilmenite FeTiO3;

_ Quadratic Rutile TiO2;

_ Quadratic Anatase TiO2;

_ Cubic Cuprite Cu2O

_ Spinels (12 main species) Cubic R_2O_3 MO

with R = Al, Fe^{3+}, Cr and M = Mg, Fe^{2+}, Zn, Mn

Cubic Chromite FeO Cr2O3; Cubic Magnetite FeO Fe2O3 (Fe_3O_4)

Hydroxides:

_ Hexagonal Brucite Mg(OH)2;

_ Monoclinic Gibbsite $Al(OH)_3$;

_ Orthorhombic Diaspore AlO2H;

_ Orthorhombic Goethite FeO(OH);

Example of Oxides: Corundum, Oligist, Magnetite.

Corundum (Al_2O_3) Corundum is a mineral species composed of recrystallized anhydrous aluminum oxide. Some natural varieties of corundum are precious stones: ruby and sapphire which oxide with aluminum. The rock powder containing this mineral, emery (metamorphic rock) was widely used in industry, mainly as an abrasive due to its hardness. The hardness of corundum is in fact 9 on the Mohs scale, making it the second hardest natural mineral after diamond. However, emery has nowadays lost its importance with the development of other types of abrasives, in particular silicon or tungsten carbides.

Hematite or Oligist (Fe_2O_3) Hematite is a mineral species composed of iron (III) oxide. This is the most common form of iron ore. It is a very common mineral, black to silver gray, brown to red, or red in color, with many crystal forms. Often, hematite is

Figure 42. Corundum and Hematite

in the form of oolites (Oolitic Oligist). Hematite weathers into brown hematite (iron hydroxide). In ancient Egypt, hematite was considered to have the power to cure blood diseases (This mineral composed mainly of iron has the particularity of tinting water red. This is why the Egyptians believed that it favored blood production).

Magnetite (Fe_3O_4) Magnetite is present in rocks of very diverse origins (magmatic, metamorphic, and sedimentary). It is an iron oxide with magnetic properties (natural magnet); It is one of the main iron ores. Colorant: primary pigment for umber and sienna. Main component of ferrite powder used for the manufacture of magnets. Dating lava flows due to its ferrimagnetic properties, it records variations in the orientation of the earth's magnetic field. we were able to determine on closely spaced castings that with each inversion of the earth's dipole there is a transition phase of 1000 years where the magnetic field can be reversed in 3 days. Biology: The pigeon would have magnetite, present in three very distinct places and in different quantities, inside its beak, which would help it to navigate in flight.

Example of Oxides: Goethite, Gibbsite.

Goethite (FeOOH) Goethite is a mineral species, a variety of iron(III) oxide hydroxide. In localities where it is abundant, goethite constitutes a very interesting mineral for the extraction of iron. Earthy varieties, such as ocher, are used as pigments. It was used as a pigment in the paintings of the Lascaux cave

Gibbsite ($Al(OH)_3$) : Gibbsite is a mineral species with the chemical formula $Al(OH)_3$, of variable color (white; gray white; grayish; greenish; greenish white; reddish; creamy white). is an important aluminum ore and one of the three mineral compounds that constitute bauxite with boehmite (AlO(OH)) and diaspore (AlO(OH)). Bauxite is a white, red or gray rock, characterized by its high content of alumina Al_2O_3 and iron oxides. This rock constitutes the main ore allowing the production of aluminum.

2.3. Sulphides And Sulfosels:

In this class, there are approximately 350 minerals. In the subclass of sulfides, we find sulfides, selenides, tellurides, arsenides and antimonides of the following metals: Ag, As, Bi, Cd, Co, Cu, Fe, Ge, Hg, Mn, Mo, Ni, Pb, Pt, Sb, Sn, Tl, V, W and Zn. In the subgroups of sulfosalts, we find sulfo-arsenides, sulfo-antimonides, sulfobismitides, sulfo-stannides, sulfo-germanides of the following metals: Ag, Cu, Pb, Sn, Bi, Fe, Sb, Tl. This class is one of the most important in mineralogy because it contains the basic ores of almost all metals other than Fe, Mn and light and precious metals.

Minerals in this class are generally soft and fragile, with the exception of pyrite. Most sulphides and similar compounds are found in deposits of hydrothermal origin, these minerals are also formed in biogenic environments and in conditions of anoxic diagenesis.

Sulphides:
_ Cubic Pyrite Fe_2S
_ Hexagonal Pyrrhotite FeS;
_ Quadratic Chalcopyrite $CuFeS_2$;
_ Cubic Galena PbS;
_ Blende or Cubic sphalerite $(Zn, Fe)S$;
_ Orthorhombic Marcasite FeS_2;
_ Hexagonal Cinnabar HgS;
_ Hexagonal Molybdenite MoS_2;

Sulfosalts:
_ Réalgar Monoclinic As_4S_4;
_ Monoclinic Orpiment As_2S_3;
_ Orthorhombic Stibine Sb_2S_3;

Sulfides: Realgar, Orpiment, Galena, Blende, Pyrite Sulfides are often formed by condensation of magmatic gases or sulfur gases of other origin. We distinguish the following main minerals:

Figure 43. Sulphides minerals

Realgar (As_4S_4) is a mineral species, composed of arsenic sulphide, red in color (and orange dust). Under the action of light, realgar tends to alter into para realgar, whose structure is very similar to that of orpiment (As_2S_3). Although uncommon, realgar is an important arsenic ore. It was used in pyrotechnics (fireworks) or for the production of illuminations as a yellow or red colored pigment, used by painters until the end of the 19th century.

Orpiment (As_2S_3) is also an arsenic sulphide, it is a yellow-gold color. Orpiment has been used since Antiquity by the Greeks, Romans and Egyptians as a pigment (paint, cosmetics such as funeral makeup, writing). It is no longer used as a pigment for paints due to its toxicity and low permanence. It was also used in fireworks. Today it is used industrially for the production of semiconductors and photoconductors.

Galena (PbS) is a lead sulfide. This is the most common lead ore. In crystallized form, galena has a cubic structure. Blende (ZnS) or sphalerite is a Zinc sulfide. This is the most common zinc ore. In crystallized form, blende has a cubic structure. Pyrite (FeS_2) is an iron sulphide whose crystal system is also cubic. Pyrite was exploited more as a source of sulfur than of iron. This very polluting industry, however, tends to be replaced by other processes. In 1985, 18% of sulfur was obtained from this ore. The quantity extracted is currently less than 8%, or 6.6 million tonnes extracted per year, including 6 million in China alone. In the USA during the 19th century, pyrite was called fool's gold: the ignorance and despair of many miners led them to confuse pyrite with gold because of its shine and its color. Pyrite crystals can be found in marshy mud, following the reduction of iron and the presence of H2S (hydrogen sulphide).

2.4. SULFATES:

Sulfates (about 200 species) are generally of low hardness and density. They generally have little color and all are fragile and tender. These are secondary minerals found in zones of oxidation or in evaporation deposits.

_ Monoclinic Gypsum $CaSO_4$/. $2H_2O$;
_ Orthorhombic anhydrite Ca SO_4;
_ Celestine Orthorhombic Sr SO_4;
_ Orthorhombic Barite Ba SO_4;
_ Orthorhombic Anglesite Pb SO_4.

a. Barite ($BaSO_4$) White to yellowish mineral, dense, orthorhombic system. In the petroleum industry, it is used as heavy drilling mud to increase the density of drilling fluids and prevent gas leaks. In nuclear power plants, it can also be used in the composition of concrete in order to considerably increase its density and its impenetrability to gamma rays. Opaque to X-rays, this product is used in radiography in an insoluble form to visualize the path of the food bolus in the digestive tract.

b. **Gypsum ($CaSO_4.2H_2O$)** ; Gypsum is white, grayish-white or pinkish in color. Monoclinic system. It can take on a fibrous appearance or particular shapes (sand rose). Dehydrated, fibrous white gypsum produces plaster. Alabaster is a variety of fine-grained solid gypsum

2.5. CARBONATES

Carbonates are one of the main constituents of sedimentary rocks (example: limestone). Their structure is relatively simple compared to that of silicates: negative complexes $(CO3)^{2-,}$ linked by positive ions such as Ca, Mg, Fe. In **calcite**, $CaCO_3$, the $(CO_3)^{2-}$ are linked by Ca^{2+} to form a rhombohedral structure typical of this mineral**.**

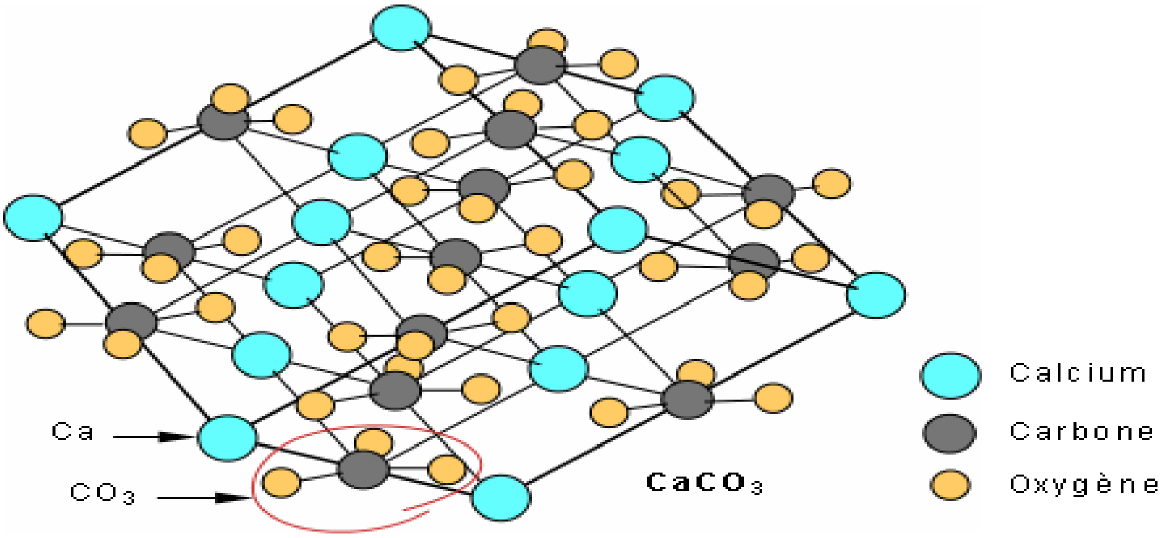


Figure 44. Rhombohedral structure typical of calcite

Carbonates have low hardness, are fragile and generally cleave easily. Most of them come into effervescence with the acids (release of carbon dioxide). Stony in appearance, they are colorless, white or lightly colored with the exception of iron, copper, cobalt, manganese, chromium and uranium carbonates. Their hardness is less than 5. Hydrated carbonates are essentially linked to the exogenous cycle. In anhydrous state, they can be found in eruptive contexts (carbonatites).

_ Rhombohedral Calcite $CaCO_3$;
_ Orthorhombic Aragonite $CaCO_3$;
_ Rhombohedral Magnesite $MgCO_3$
_ Rhombohedral Dolomite (Ca, Mg) CO_3;
_ Rhombohedral Siderite $FeCO_3$;
_ Rhombohedral Rhodocrosite $MnCO_3$.

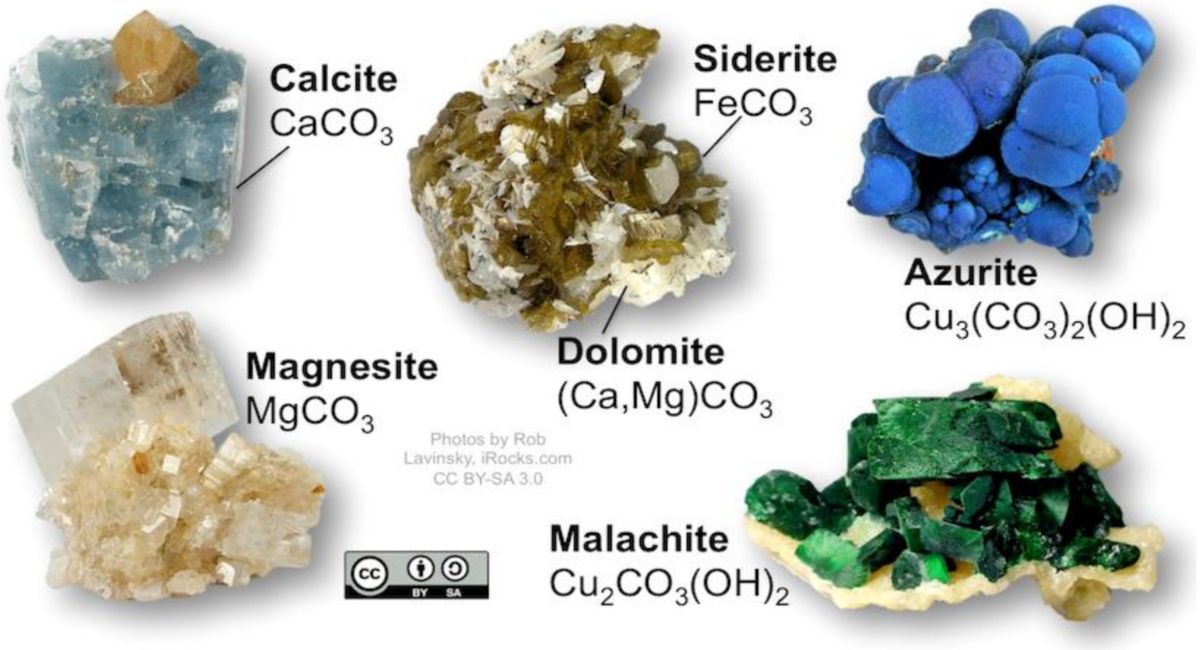


Figure 45. Carbonate minerals

a. **Calcite ($CaCO_3$)** is, after quartz, the most widespread mineral on the earth's surface and also one of the most varied minerals in terms of shape. Calcite is a mineral composed of natural calcium carbonate with the formula CaCO3, with traces of Mn, Fe, Zn, Co, Ba, Sr, Pb, Mg, Cu, Al, Ni, Cr, Mo. The abundance of cations other than calcium explains the richness of the varieties described and colors (generally white or yellowish, red, black, blue...) for this mineral. Formation after chemical precipitation during the evaporation of solutions rich in calcium bicarbonate but can also be of organogenic origin. It is a major component in limestones. It is a transparent to translucent mineral, more rarely opaque. It reacts strongly to hydrochloric acid even when cold.

b. **ARAGONITE ($CaCO_3$)** Less common than calcite, aragonite is a mineral (colorless, white-gray to pale yellow or shades of blue, green, purple or red; orthorhombic system) which is mainly found in low temperature deposits formed near the land surface (stalactites and stalagmites of caves, oxidation zones of mineral deposits, hot springs). Aragonite is rarer than calcite. In many organisms, the original shell (shell), formed of aragonite, is then transformed into calcite. (Under ambient conditions, aragonite transforms very slowly into calcite over several tens or even hundreds of millions of years). Pearls and mother-of-pearl (Nacre is the interior coating of certain mollusk shells) are made up of lamellae of aragonite mixed with organic matter. It crystallizes well in waters rich in sodium chloride. It plays a major role in the biogeochemical carbon cycle and in oceanic carbon sinks. Aragonite becomes soluble in the ocean beyond a certain acidity of the water (slightly variable depending on the temperature), which is why it is considered one of the tracers and indicators of induced ocean acidification by anthropogenic emissions of CO_2 in particular. Depending on the species, the shell or exoskeleton of many marine organisms is made of aragonite or calcite or a superposition or mixture of these two crystalline forms. The more acidic the water, the more competition there will be between the biochemical construction of limestone and its chemical dissolution in the ambient seawater. In water that is too acidic, already formed shells can disintegrate, killing the animals they were protecting.

C**. DOLOMITE ($CaMg(CO_3)_2$)** When the waters become magnesian, we no longer have precipitation of calcite only, but also of dolomite. Dolomite reacts to HCL very weakly or not at all when cold, more strongly if the mineral is heated. Rhombohedral crystal system, variable color. Mineral in association with calcite to form dolomite.

2.6. PHOSPHATES and NITRATES:

2.6.1. PHOSPHATES

These minerals are most often very colorful and sometimes form big crystals. These are accessory minerals of magmatic and metamorphic rocks.

_ Hexagonal Apatite $Ca_5(PO_4)_3$ (OH, F, Cl);
_ Monoclinic Monazite (Ce, La, Th) PO_4;
_ Quadratic xenotime $(PO_4)Y$;
_ Orthorhombic Variscite Al (PO_4), $2H_2O$;

Figure 46. Hexagonal Apatite cristal

Apatite is a generic name designating hexagonal phosphates (hexagonal crystal system) of fairly variable composition, $Ca_5(PO_4)_3(OH, Cl, F)$. Three species are very well known: Chlorapatite $Ca_5(PO_4)_3Cl$, Fluorapatite$Ca_5(PO_4)_3F$

Hydroxyapatite $Ca_5(PO_4)_3(OH)$; Apatite is found in sedimentary, metamorphic and magmatic rocks. Sedimentary apatites are of chemical and/or organogenic (biochemical) origin: the “raw” raw material for the phosphorus industry is phosphorite, a phosphorous sedimentary rock whose main component is carbonato-fluorapatite. Hydroxyapatite is the main mineral, which is part of the composition of bone and dental tissues. Vertebrate skeletons can form phosphate sediments (Calcium phosphate is soluble in an acidic environment (river), but much less so in an alkaline environment (sea). The change in pH when a river flows into the sea produces precipitation phosphate, which contributes to the murky waters of estuaries.). Apatite is therefore a source of phosphorus to make artificial fertilizers.

2.6.2. NITRATES:

Nitrate minerals are used to make fertilizers and nitric acid. Niter and nitratin are evaporites, meaning they crystallize following the evaporation of water in which these minerals are soluble.

a. Nitratine ($NaNO_3$) White or reddish in color, nitratine has a primitive rhombohedral crystalline shape. Very soluble in water, it is found in dry regions such as deserts following the evaporation of water brought by rivers. For example, they are found in the desert regions west of the Andes mountain range in Chile; or even in Death Valley in the USA. Mixed with other salts, nitratine produces “Chile Caliche” which is used to make fertilizer.

b. Niter (KNO_3) Niter forms saltpeter, which was formerly used as an explosive or in the manufacture of fertilizer. On the surface of damp cellar walls, we can observe the formation of this mineral. Saltpeter is also used in the preservation of meat and cold meats. This is the additive E252. It reacts and produces nitrite then nitrogen monoxide which transforms red myoglobin into a pink coloring typical of ham and salamis.

2.7. HALIDES:

Some 130 minerals belong to this class. Anions are represented by the halogen elements: F, Cl, Br, and I. Chlorides (Cl) and fluorides (F) are the most common compounds in this class. The physical properties common to these halides are their low brittleness, hardness and density. These minerals are often soluble in water. They are found in evaporitic sediments and volcanic emanations sublimated from fumaroles.

_ Cubic Fluorite CaF_2;

_ Halite Cubic NaCl;

_ Sylvite Cubic KCl.

Halides are minerals containing elements from the halogen group (Br, Cl, F).

Figure 47. Halides minerals

a. **Halite (NaCl)** is a mineral with a cubic structure composed of sodium chloride with the formula NaCl with traces of iodine, bromine, fluorine, iron, and silicon. Pure, it is colorless if the crystals are well formed, or white. The presence of impurities sometimes gives it a gray, yellowish to reddish, brownish color. Halite is a component of many evaporitic rocks, originating from the evaporation of salty subsea lakes. It can be found in large layers in sedimentary deposits and in efflorescences in arid regions.

Its main uses are:□ore for the extraction of soda and hydrochloric acid;□in the food industry, as a preservative (especially for preserving meat) or condiment (food salt);□halite is the main constituent of salt used for road salting;□important mineral for the extracted by-products: potash, magnesium, chlorine, bromine, iodine.

b. Sylvine (KCl) is a mineral species (cubic system like halite) of the chloride family. This is the mineralogical form of potassium chloride with the formula KCl. Very soluble in water like halite, it is distinguished by its very bitter taste on the tongue. It is also a component of evaporitic sedimentary rocks. Sylvine is used to make potash fertilizers.

c. **Fluorine (CaF_2)** or fluorite is a mineral species composed of calcium fluoride, with the formula CaF_2. The color is variable: colorless, green, pink, purple, blue...It is fluorescent when illuminated by a ultraviolet radiation. Its name comes from the Latin fleure which means fondant (flowing). It is in fact used as a flux (allows the melting point of metals to be lowered) by steel and glass manufacturers, it is also used in the manufacture fiberglass and especially for the production of hydrofluoric acid and fluorinated derivative products, including aluminum fluoride, from which aluminum metal is obtained. Calcium fluoride is also used in instrumental optics.

2.8. BORATES

The **Borate Minerals** are minerals which contain a borate anion group. **boron (B)**, chemical element, semimetal of main Group 13 (IIIa, or boron group) of the periodic table, essential to plant growth and of wide industrial application The borate (BO_3) units may be polymerised similar to the SiO_4 unit of the silicate mineral class. This results in B_2O_5, B_3O_6, B_2O_4 anions as well as more complex structures which include hydroxide or halogen anions. The $[B(O,OH)_4]^-$ anion exists as well. Borate mineral structures incorporate either the BO_3 triangle or BO_4 tetrahedron in which oxygen or hydroxyl groups are located at the vertices of a triangle or at the corners of a tetrahedron with a central boron atom, respectively. Both types of units may occur in one structure. Vertices may share an oxygen atom to form extended boron–oxygen networks, or if bonded to another metal ion consist of a hydroxyl group. The size of the boron–oxygen complex in any one mineral generally decreases with an increase of the temperature and pressure at which the mineral forms. Many borate minerals, such as borax, colemanite, and ulexite, are salts: soft, readily soluble, and found in evaporite contexts. However, some, such as boracite, are hard and resistant to weathering, more similar to the silicates. There are over 100 different borate minerals.

Figure 48. Boracite and Borax Cristals

Table 8. Principal Borate minerals and teir physical properities

Name	Colour	Lustre	Mohs hardness	specific gravity
boracite **$Mg_3B_7O_{13}Cl$**	colourless or white	Vitreous	7–7½	2.9–3.0
Borax	colourless to white; grayish, bluish, greenish	vitreous to resinous	2–2½	1.7
colemanite **$Ca_2B_6O_{11}.5H_2O$**	colourless; white, yellowish, gray	brilliant vitreous to adamantine	4½	2.4
inyoite **$Ca_2B_6O_{11}.\ 13H_2O$**	colourless, becoming white and cloudy after partial dehydration	Vitreous	2	1.7
Kernite	Colourless	Vitreous	2½	1.9
Ludwigite	dark green to coal black	Silky	5	3.6 (lud) to 4.7 (paig)
Priceite	White	Earthy	3–3½	2.4
Sussexite	white to straw-yellow	silky to dull or earthy	3–3½	2.6 (szai) to

				3.3 (suss)
Tincalconite **$Na_2B_40_7.5H_2O$**	white (natural); colourless (artificial)	Vitreous		1.9
Ulexite **$NaCaB_50_9.8H_2O$**	colourless; white	vitreous; silky or satiny	2½	2.0

	Habit or Form	**Fracture or Cleavage**	**Crystal system**
Boracite	isolated, embedded, cubelike crystals	conchoidal to uneven fracture	orthorhombic (isometric above 265 degrees C)
Borax	short prismatic crystals	one perfect, one good cleavage	Monoclinic
Colemanite	short prismatic crystals; massive	one perfect, one distinct cleavage	monoclinic
Inyoite	short prisms and coarse crystal aggregates; geodes; drusy crusts; granular massive	one good cleavage	monoclinic
Kernite	very large crystals; fibrous, cleavable, irregular masses	two perfect cleavages	monoclinic
Ludwigite	fibrous masses; rosettes; sheaflike aggregates	no observed cleavage	orthorhombic
Priceite	soft and chalky to hard and tough nodules	earthy to conchoidal	triclinic
Sussexite	fibrous or felted masses or veinlets; nodules		orthorhombic
Tincalconite	found in nature as a fine-grained powder; physical properties are given for artificial pseudocubic crystals	hackly fracture	hexagonal
Ulexite	small nodular, rounded, or lenslike crystal aggregates; fibrous botryoidal crusts;	one perfect, cleavage	orthorhombic

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