

EENS 211	Mineralogy
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Silicate Structures, Structural Formula, Neso-, Cyclo-, and Soro- Silicates	

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Silicate Structures and Structural Formula

As we discussed in a previous lecture, the relative abundance of elements in the Earth's crust determines what minerals will form and what minerals will be common. Because Oxygen and Silicon are the most abundant elements, the silicate minerals are the most common. Thus, we will spend some time here discussing the structure, chemistry, and occurrence of silicate minerals. Our systematic discussion of the common rock forming minerals will follow in the lectures throughout the remainder of the course.

Element	Wt%	Atomic%	Volume%
O	46.60	62.55	~94
Si	27.72	21.22	~6
Al	8.13	6.47	
Fe	5.00	1.92	
Ca	3.63	1.94	
Na	2.83	2.34	
K	2.59	1.42	
Mg	2.09	1.84	
Total	98.59	100.00	100

In order to discuss the silicates and their structures it is first necessary to remember that the way atoms are packed together or coordinated by larger anions, like oxygen depends on the radius ratio of the cation to the anion, R_x/R_z .

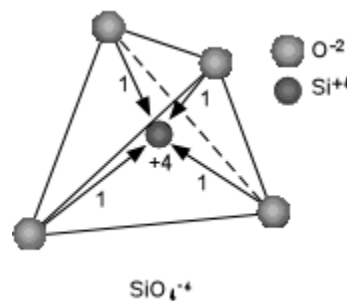
R_x/R_z	C.N.	Type
1.0	12	Hexagonal or Cubic Closest Packing
1.0 - 0.732	8	Cubic
0.732 - 0.414	6	Octahedral
0.414 - 0.225	4	Tetrahedral
0.225 - 0.155	3	Triangular
<0.155	2	Linear

Since oxygen is the most abundant element in the crust, oxygen will be the major anion that coordinates the other other cations. Thus, for the major ions that occur in the crust, we can make the following table showing the coordination and coordination polyhedra that are expected for each of the common cations.

Ion	C.N. (with Oxygen)	Coord. Polyhedron	Ionic Radius, Å
K ⁺	8 - 12	cubic to closest	1.51 (8) - 1.64 (12)
Na ⁺	8 - 6	cubic to octahedral	1.18 (8) - 1.02 (6)
Ca ⁺²	8 - 6		1.12 (8) - 1.00 (6)
Mn ⁺²	6	Octahedral	0.83
Fe ⁺²	6		0.78
Mg ⁺²	6		0.72
Fe ⁺³	6		0.65
Ti ⁺⁴	6		0.61
Al ⁺³	6		0.54
Al ⁺³	4	Tetrahedral	0.39
Si ⁺⁴	4		0.26
C ⁺⁴	3	Triangular	0.08

The radius ratio of Si⁺⁴ to O⁻² requires that Si⁺⁴ be coordinated by 4 O⁻² ions in tetrahedral coordination.

In order to neutralize the +4 charge on the Si cation, one negative charge from each of the Oxygen ions will reach the Si cation. Thus, each Oxygen will be left with a net charge of -1, resulting in a SiO₄⁻⁴ tetrahedral group that can be bonded to other cations. It is this SiO₄⁻⁴ tetrahedron that forms the basis of the silicate minerals.



Since Si⁺⁴ is a highly charged cation, Pauling's rules state that it should be separated as far as possible from other Si⁺⁴ ions. Thus, when these SiO₄⁻⁴ tetrahedrons are linked together, only corner oxygens will be shared with other SiO₄⁻⁴ groups. Several possibilities exist and give rise to the different silicate groups.

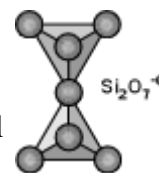
Nesosilicates (Island Silicates)

If the corner oxygens are not shared with other SiO₄⁻⁴ tetrahedrons, each tetrahedron will be isolated. Thus, this group is often referred to as the island silicate group. The basic structural unit is then SiO₄⁻⁴. In this group the oxygens are shared with octahedral groups that contain other cations like Mg⁺², Fe⁺², or Ca⁺². Olivine is a good example: (Mg,Fe)₂SiO₄.



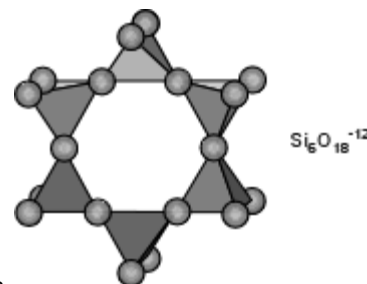
Sorosilicates (Double Island Silicates)

If one of the corner oxygens is shared with another tetrahedron, this gives rise to the sorosilicate group. It is often referred to as the double island group because there are two linked tetrahedrons isolated from all other tetrahedrons. In this case, the basic structural unit is $\text{Si}_2\text{O}_7^{-6}$. A good example of a sorosilicate is the mineral hemimorphite - $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})\cdot\text{H}_2\text{O}$. Some sorosilicates are a combination of single and double islands, like in epidote - $\text{Ca}_2(\text{Fe}^{+3},\text{Al})\text{Al}_2(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{OH})$.



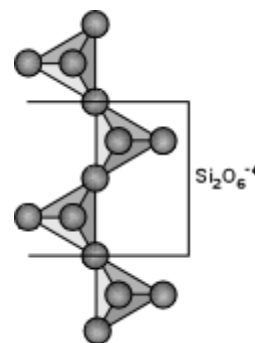
Cyclosilicates (Ring Silicates)

If two of the oxygens are shared and the structure is arranged in a ring, such as that shown here, we get the basic structural unit of the cyclosilicates or ring silicates. Shown here is a six membered ring forming the structural group $\text{Si}_6\text{O}_{18}^{-12}$. Three membered rings, $\text{Si}_3\text{O}_9^{-6}$, four membered rings, $\text{Si}_4\text{O}_{12}^{-8}$, and five membered rings $\text{Si}_5\text{O}_{15}^{-10}$ are also possible. A good example of a cyclosilicate is the mineral Beryl - $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$.



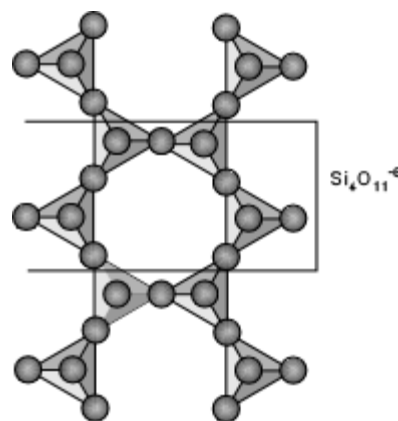
Inosilicates (Single Chain Silicates)

If two of the oxygens are shared in a way to make long single chains of linked SiO_4 tetrahedra, we get the single chain silicates or inosilicates. In this case the basic structural unit is $\text{Si}_2\text{O}_6^{-4}$ or SiO_3^{-2} . This group is the basis for the pyroxene group of minerals, like the orthopyroxenes (Mg,Fe) SiO_3 or the clinopyroxenes $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$.



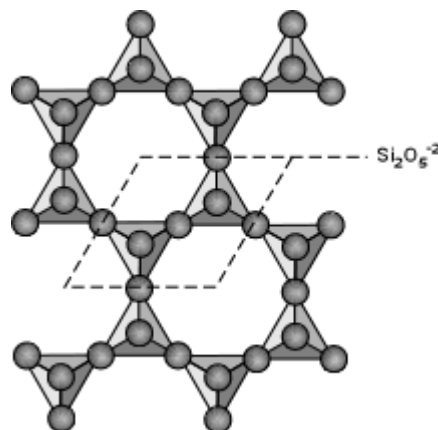
Inosilicates (Double Chain Silicates)

If two chains are linked together so that each tetrahedral group shares 3 of its oxygens, we can form double chains, with the basic structural group being $\text{Si}_4\text{O}_{11}^{-6}$. The amphibole group of minerals are double chain silicates, for example the tremolite - ferroactinolite series - $\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$.



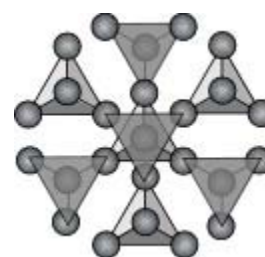
Phyllosilicates (Sheet Silicates)

If 3 of the oxygens from each tetrahedral group are shared such that an infinite sheet of SiO_4 tetrahedra are shared we get the basis for the phyllosilicates or sheet silicates. In this case the basic structural group is $\text{Si}_2\text{O}_5^{-2}$. The micas, clay minerals, chlorite, talc, and serpentine minerals are all based on this structure. A good example is biotite - $\text{K}(\text{Mg,Fe})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$. Note that in this structure, Al is substituting for Si in one of the tetrahedral groups.



Tectosilicates (Framework Silicates)

If all of the corner oxygens are shared with another SiO_4 tetrahedron, then a framework structure develops. The basic structural group then becomes SiO_2 . The minerals quartz, cristobalite, and tridymite all are based on this structure. If some of the Si^{+4} ions are replaced by Al^{+3} then this produces a charge imbalance and allows for other ions to be found coordinated in different arrangements within the framework structure. Thus, the feldspar and feldspathoid minerals are also based on the tectosilicate framework.

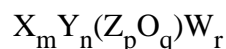


General Formula for Silicates

Based on these basic structural units, we can construct a general structural chemical formula for the silicates. But one substitution in particular tends to mess things up a bit. This is Al^{+3} , the third most abundant element in the Earth's crust. Al^{+3} has an ionic radius that varies between 0.54 and 0.39 depending on the coordination number. Thus, it could either fit in 6-fold coordination with oxygen or 4-fold coordination with oxygen. Because Al^{+3} will go into 4-fold coordination with oxygen, it sometimes substitutes for Si^{+4} . If such a substitution takes place, it creates a charge imbalance that must be made up elsewhere in the silicate structure.

The other common elements in the Earth's crust that enter the silicates do so in other types of coordination. Ions like Al^{+3} , Mg^{+2} , Fe^{+2} , Fe^{+3} , Mn^{+2} , and Ti^{+4} enter into 6-fold or octahedral sites. Larger ions like Ca^{+2} , and Na^{+1} , are found in octahedral coordination or 8-fold, cubic coordination sites. Very large cations like K^{+1} , Ba^{+2} , and sometimes Na^{+1} are coordinated by 12 oxygens in 12-fold coordination sites.

We can thus write a general structural formula for the silicates as follows:



where X represents an 8 to 12 fold coordination site for large cations like K^+ , Rb^+ , Ba^{+2} , Na^+ , and Ca^{+2} .

Y represents a 6-fold (octahedral) site for intermediate sized cations like Al^{+3} , Mg^{+2} , Fe^{+2} , Fe^{+3} , Mn^{+2} , and Ti^{+4} .

Z represents the tetrahedral site containing Si^{+4} , and Al^{+3} .

the ratio p:q depends on the degree of polymerization of the silica (or alumina) tetrahedrons, or the silicate structural type as discussed above.

O is oxygen,

and W is a hydroxyl (OH^{-1}) site into which can substitute large anions like F^{-1} or Cl^{-1} .

The subscripts m, n, and r depend on the ratio of p to q and are chosen to maintain charge balance.

This is summarized in the table shown here. In this table note that there is very little substitution that takes place between ions that enter the X, Y, and Z sites. The exceptions are mainly substitution of Al^{+3} for Si^{+4} , which is noted in the Table, and whether the X site is large enough to accept the largest cations like K^{+1} , Ba^{+2} , or Rb^{+1} .

Site	C.N.	Ion
Z	4	Si^{+4}
		Al^{+3}
Y	6	Al^{+3}
		Fe^{+3}
		Fe^{+2}
		Mg^{+2}
		Mn^{+2}
		Ti^{+4}
X	8	Na^{+1}
		Ca^{+2}
	8 - 12	K^{+1}
		Ba^{+2}
		Rb^{+1}

Nesosilicates (Island Silicates)

We now turn our discussion to a systematic look at the most common rock forming minerals, starting with the common nesosilicates. Among these are the olivines, garnets, Al_2SiO_5 minerals, staurolite, and sphene (the latter two will be discussed in the last lecture on accessory minerals).

As discussed above, the nesosilicates or island silicates are based on the isolated SiO_4^{-4} tetrahedral groups. In the olivines, the remaining corner oxygens form octahedral groups that coordinate Mg^{+2} and Fe^{+2} ions.



Olivines

The olivines consist of a complete solid solution between Mg_2SiO_4 (forsterite, Fo) and Fe_2SiO_4 (fayalite, Fa). There is limited substitution of the following end members:

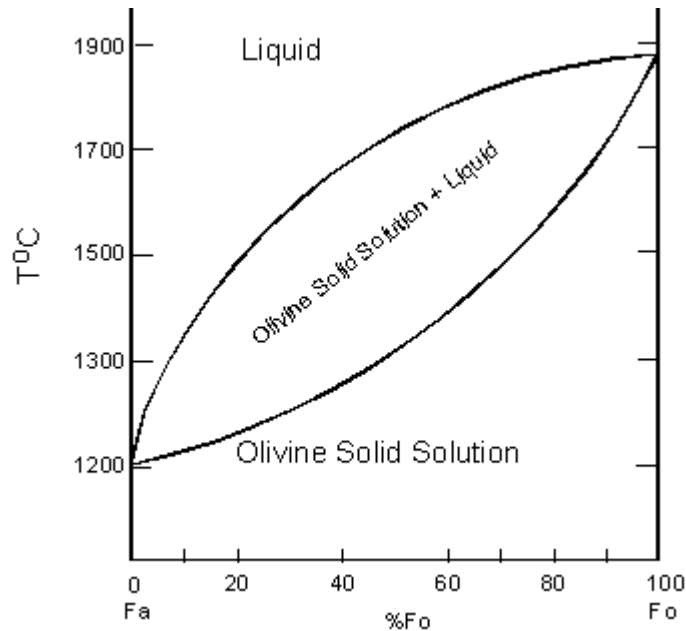
Ca_2SiO_4 - larnite

Mn_2SiO_4 - tephroite

CaMgSiO_4 - monticellite (which is commonly found in metamorphosed dolomites)

Also found substituting in octahedral sites are Ni^{+2} and Cr^{+3} , particularly in Mg-rich olivines.

The phase diagram for the common end members of the olivine solid solution series shows that pure forsterite melts at 1890°C and pure fayalite melts at 1205°C . Thus, the olivines are sometimes seen to be zoned from Mg-rich cores to more Fe-rich rims, although such zoning is usually limited to 5 to 10% difference between the cores and the rims.



- Occurrence

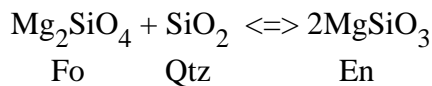
Pure forsterite is limited to metamorphosed Mg-rich limestones and dolomitic metamorphic rocks.

Fo_{90-95} is found in ultrabasic igneous rocks, particularly dunites (>90% by volume olivine), and peridotites (Olivine + Cpx + Opx).

Fo_{60-90} is found in basic igneous rocks like basalts and gabbros, and sometimes in andesites, where it occurs with plagioclase and pyroxene.

Fa_{100-40} is found in Fe-rich siliceous igneous rocks like rhyolites and granites.

Mg-rich olivines rarely occur in quartz bearing rocks and quartz rarely occurs with Mg-rich olivine because the reaction shown below runs to the right for most pressures and temperatures.



Note however, that Fe-rich olivines can occur with quartz.

- Structure

The structure of the olivines is illustrated on page 439 of Klein and Dutrow. Note that 2 different kinds of octahedral sites occur. One is a regular octahedron, labeled M2, and the other is a distorted octahedron, labeled M1. Fe^{+2} and Mg^{+2} have no particular preference for either site, but if Ca^{+2} is present it prefers the M2 site.

- Identifying Properties

The olivines are orthorhombic (2/m2/m2/m) and usually green colored in hand specimen.

The most characteristic property in thin section is their surface texture that kind of looks like a piece of sandpaper (see photo on the back wall of the Mineralogy lab).

Because of their good {010} cleavage and common {100} parting, they show parallel extinction relative to the cleavage or parting.

Maximum birefringence as seen in the interference colors in thin section varies between 3rd order blue (for Fo rich varieties) and 3rd order yellow (for Fa-rich varieties), but remember that this is the maximum birefringence that will only be seen for grains with α and γ parallel to the microscope stage.

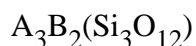
Fo-rich olivines are usually clear in thin section, but Fa-rich olivines show pale yellow, greenish yellow, or yellow amber absorption colors and sometimes show pleochroism with $\alpha = \gamma$ = pale yellow, β = orange, yellow, or reddish brown.

Because optical properties vary with composition of the olivine, 2V is useful in distinguishing olivine compositions. Look at the graph on page 11 of Deer, Howie, and Zussman. From the graph you can see that very Fo-rich olivines(>Fo₉₀) are optically positive with a 2V between 82 and 90°. Between Fo₉₀ and Fa₁₀₀ the olivine is optically negative with 2V _{γ} between 90 and 130 (2V between 90° and 50°). Thus, by estimating the 2V, you should be able to estimate the composition of the olivine.

Olivines are distinguished from orthorhombic pyroxenes (opx) easily because olivines show higher maximum birefringence and do not show the characteristic {110} cleavage of the pyroxenes. They are distinguished from the clinopyroxenes (Cpx) which show inclined extinction relative their {110} cleavage and show a biaxial positive character with a 2V of 50 to 60°.

Garnets

Garnets are isometric minerals and thus isotropic in thin section, although sometimes they are seen to be weakly birefringent (slightly anisotropic). They are also nesosilicates, and therefore based on the SiO₄ structural unit. The general formula for garnets is:



where the A sites are cubic sites containing large divalent cations, usually Ca, Fe, Mg, or Mn, and the B sites are octahedral sites occupied by smaller trivalent cations, like Al and Fe⁺³.

Garnets with no Ca in the A site and Al in the B site are called the pyrospite series. These consist of the end members:

Pyrope - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

Almandine - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

Spessartine - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

Garnets with Ca in the A site are called the ugrandite series and consist of the end members:

Uvarovite - $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$

Grossularite - $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

Andradite - $\text{Ca}_3\text{Fe}^{+3}_2\text{Si}_3\text{O}_{12}$

Limited solid solution exists between end members of each series.

- Occurrence

The garnets occur mostly in metamorphic rocks where they are often seen to form euhedral (well-formed) crystals.

The Mg-rich garnet, pyrope, is found in metamorphic rocks formed at high pressure and in eclogites (basalts metamorphosed at high pressure) and peridotites (ultrabasic rocks containing olivine, Opx, Cpx, and garnet).

The Fe-rich garnet, almandine, is the most common garnet and is found in metamorphic aluminous schists.

The Mn-rich variety, spessartine, is limited to Mn-rich metamorphic rocks like meta-cherts.

- Identifying Properties

Garnets are generally isotropic although some may be weakly birefringent. In hand specimen they exhibit a wide range of colors and these are sometimes seen in thin section. Color is controlled by the amounts of Fe^{+2} , Fe^{+3} , Mg^{+2} , and Cr^{+3} present.

Pyrope is usually pinkish red to purplish in hand specimen and is usually clear in thin section.

Almandine is usually deep red to brownish black in hand specimen and pink in thin section.

Spessartine ranges from black to red to brown and orange and is usually pink in thin

section.

Grossularite has a color in hand specimen that reflects the amount of Fe and Mn present and thus ranges from brown to yellow to pink. If Cr is present, the color is usually green. In thin section grossularite varies in color from clear to brown or green in Cr-rich varieties.

Uvarovite, with high Cr concentration is usually deep green in hand specimen and green in thin section.

Andradite ranges from yellow to dark brown, but if appreciable amounts of Ti are present, the color could be black in hand specimen and brown in thin section.

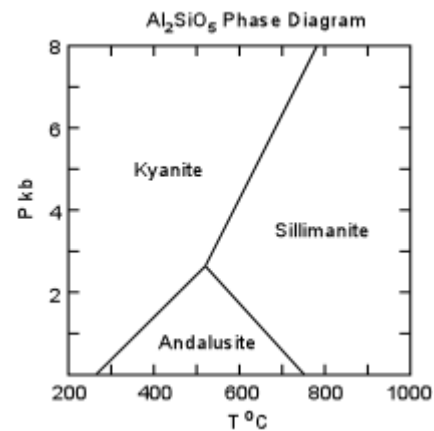
The composition and identity of the garnets is best determined either by association with other minerals or by more sophisticated techniques such as electron microprobe or XRD.

Garnets are easily distinguished from other minerals by their high relief, isotropic character, and common euhedral habit.

Al_2SiO_5 Minerals

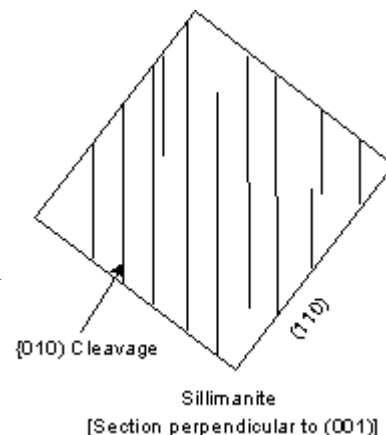
The Al_2SiO_5 minerals are common in aluminous metamorphic rocks (meta-shales and meta-mudstones) and sometimes found in aluminous igneous rocks.

In metamorphic rocks the Al_2SiO_5 polymorphs provide rather general estimates of the pressure and temperature of metamorphism, with Kyanite indicating relatively high pressure, andalusite indicating low temperature and pressure, and sillimanite indicating high temperature. Better estimates of pressure and temperature are provided if two of the minerals are present in the same rock.



- Sillimanite

Sillimanite is orthorhombic with a good {010} cleavage. It generally occurs in long fibrous crystals that are length slow, with extinction parallel to the {010} cleavage. In sections lying on {001} that show well-developed {110} forms, the cleavage is usually seen to cut across the crystal as shown here. Maximum birefringence is generally seen to be between 2° yellow to 2° red. Sillimanite is biaxial positive with a 2V of 21 - 31°.



- Andalusite

Andalusite is also orthorhombic, but shows a length fast character. It generally tends to occur as euhedral blocky crystals with a maximum birefringence in thin section between 1° yellow and 1° red. It sometimes shows weak pleochroism with α = rose-pink, $\beta = \gamma$ = greenish yellow. Some varieties show a cross, termed the chiastolite cross, which is made up of tiny carbonaceous inclusions oriented along crystallographic directions (see illustration on page 492 of Klein & Dutrow). Andalusite generally occurs as euhedral crystals with an almost square prism. It is biaxial negative with $2V = 73 - 86^\circ$.

- Kyanite

Kyanite is triclinic and thus shows inclined extinction relative to its good {100} and {010} cleavages and {001} parting. In hand specimen kyanite is commonly pale blue in color, but is clear to pale blue in thin section. Because of its good cleavages and parting, two cleavages or partings are seen in any orientation of the crystal in thin section. These cleavages intersect at angles other than 90° and thus look like parallelograms in two dimensions. Because Kyanite has high relief relative to other minerals with which it commonly occurs, it stands out in thin section and sometimes appears to have a brownish color. This color is more due to its high relief and numerous cleavages rather than due to selective absorption.

Kyanite is biaxial negative with $2V = 78 - 83^\circ$

Sorosilicates

Sorosilicates are the double island silicates. Only one important mineral group, the epidote group, has this structure.

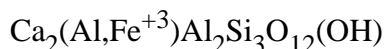
Epidote, Clinozoisite, Zoisite

The important minerals in the epidote group are epidote, clinozoisite, and zoisite. Since the sorosilicates are based on the $\text{Si}_2\text{O}_7^{-6}$ group, the structural formula can be written as:

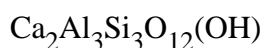


Thus, the epidote group contains both the double tetrahedra and the single tetrahedron, separated by groups of AlO_6 octahedra and Ca in nine to 10 fold coordination with Oxygen or OH.

The formula can be rewritten as:



Epidote is the Fe-rich variety and has the above general formula. Clinozoisite is the Fe-free variety with the chemical formula:



Both clinozoisite and epidote are monoclinic (2/m). Zoisite has the same chemical formula as clinozoisite, but is orthorhombic.

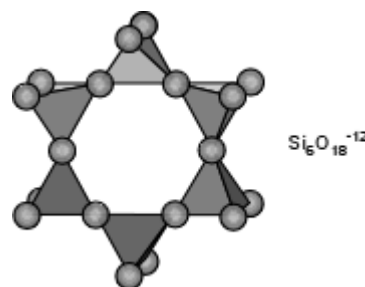
Epidote is usually pistachio green in color with perfect {001} cleavage and imperfect {100} cleavage. It is optically negative with a 2V of 64 - 90°. It usually shows pleochroism with α - colorless to pale yellow, β - greenish yellow, and γ - yellowish green, and shows high relief relative to feldspars and quartz. Its birefringence is high enough to show 3rd order interference colors. It usually shows an anomalous blue extinction.

Clinozoisite shows similar relief and cleavage to epidote, but it is optically negative with a 2V of 14 to 90°, shows no pleochroism, and lower birefringence (1st to 2nd order interference colors). Zoisite is similar to clinozoisite, except it will show parallel extinction relative to faces parallel to the crystallographic axes.

Epidote is a common mineral in low grade metamorphic rocks, particularly metamorphosed volcanic rocks and Fe-Al rich meta shales. Both Clinozoisite and epidote occur as alteration products of plagioclase and as veins in granitic rocks.

Cyclosilicates

The cyclosilicates are based on rings of SiO_4 tetrahedra, with a Si:O ratio of 1:3. The most common minerals based on this structure are Beryl, Cordierite, and Tourmaline.



Beryl

$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ is hexagonal (6/m2/m2/m) with a strong prismatic habit with the form {10 $\bar{1}$ 0} usually the only form present. It is usually deep green to yellowish green in color. Beryl forms different gemstones depending on color - Aquamarine when it is pale greenish-blue, Morganite if pink, and emerald if deep green and transparent. Beryl is a common constituent of coarse grained granitic rocks and pegmatites and is found in aluminous mica schists.

In thin section, Beryl shows higher relief than quartz, and is distinguished from quartz by its negative optic sign and length-fast character. The only other mineral that it can be confused with is apatite, but apatite shows even higher relief than Beryl.

Cordierite

Cordierite is $(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot n\text{H}_2\text{O}$. It is orthorhombic (2/m2/m2/m), but shows a pseudohexagonal character due to its common cyclical twinning on {110}. In thin section it may show a twinning that looks like albite twinning, which makes it hard to distinguish from plagioclase. But, cordierite is usually dusted with tiny opaque inclusions. In thick sections it shows a pale -yellow, violet, pale blue pleochroism. It can be distinguished from quartz by its biaxial character.

Cordierite is a common constituent of aluminous metamorphic rocks. It is common in contact metamorphic rocks where it is commonly associated with sillimanite or andalusite, feldspars and micas.

Tourmaline

Tourmaline - $\text{Na}(\text{Mg,Fe,Mn,Li,Al})_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_4$ is hexagonal (3m) and is commonly found as well-formed prismatic crystals, with a rounded triangular cross section perpendicular to the c crystallographic axis.

Tourmaline is a common mineral in pegmatites (SiO_2 - rich igneous rocks with large grain size), where it is associated with quartz and alkali feldspar. It is also found in metasomatized rocks of all types, where it is precipitated from a Boron and Silica - rich fluid phase.

It's most distinguishing properties are its uniaxial negative optical character and its pleochroism with ω = dark green or dark blue and ε = yellow or violet. Tourmaline usually forms in euhedral crystals with well developed prism faces and extinction parallel to the prism faces.

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