Subject	Geology
Paper No and Title	**Crystallography and Mineralogy**
Module No and Title	Alumino-silicate Group
Module Tag	Min X

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1. Learning outcomes

After studying this module you shall be able to:

- To develop a basic understanding of chemical co-ordination leading to formation of minerals with various structures.
- To develop the ability to identify minerals in hand-specimen and thin section
- To develop appreciation for the application of mineral science to everyday life.

2. The classification of alumino-silicates based on SiO_4 tetrahedron

Silicon is known to be the second most abundant element after oxygen forming the Earth's crust and mantle. Silicate minerals predominate vast majority of rocks of the Earth's crust as the Si-O bond is considered to be stronger than any other bond prevalent amongst oxygen and any other element. As the [SiO_4] tetrahedral dominate silicate structures, the way it arranges itself within a particular structure has long been the way of silicate classification. [SiO_4] tetrahedral are either isolated from each other or connected by corner sharing to other [SiO_4] tetrahedra. The different frameworks provided by variable corner sharing tetrahedra with other cations fitting into suitable interstices provided by this frame work defines the various types of silicate structures This framework of cations and [SiO_4] tetrahedra is of prime importance in understanding the way in which a mineral would adapt to changes in its physical and chemical environment. Many silicate minerals also show substitution of Al for Si in the tetrahedron which is accompanied by compensating replacement in cation content to maintain charge neutrality.

Based on [SiO_4] tetrahedra linkage the alumonisilicate minerals (kyanite, andalusite and sillimanite) with a composition AlAl (SiO_4)O are clubbed under the nesosilicates. In all the three minerals; chains of Al-O octahedral occurs parallel to the crystallographic axis, each octahedra shares two oxygens with the above and below octahedron thus giving rise to Al-O chains of AlO_4 composition. The chains are cross linked by the remaining Al and Si ions. In all cases Si is tetrahedrally coordinated by oxygen ions, resulting in discrete $(SiO_4)^{4-}$ structural units. The remaining Al ion is in 6 fold coordination in kyanite, 5 fold coordination in andalusite and 4 –fold coordination in sillimanite.

These three minerals are of same composition but exist as different structures owing to different cross linking and chain positioning depending on the temperature and pressure conditions, hence are considered polymorphs. They have been widely studied in petrology as they are useful as pressure temperature markers of metamorphism in crustal rocks.

3. Structure and chemistry

3.1 Kyanite - Greek word kyanos, dark blue substance

The structure of kyanite consists of chains of edge sharing Al-O octahedra that are linked together by the remaining Si, Al and O ions, Si being coordinated by four oxygen ions and Al by six oxygen ions. **(Fig.1)** Kyanite has a relatively dense structure in which oxygen atoms are arranged in slightly distorted cubic close packing.

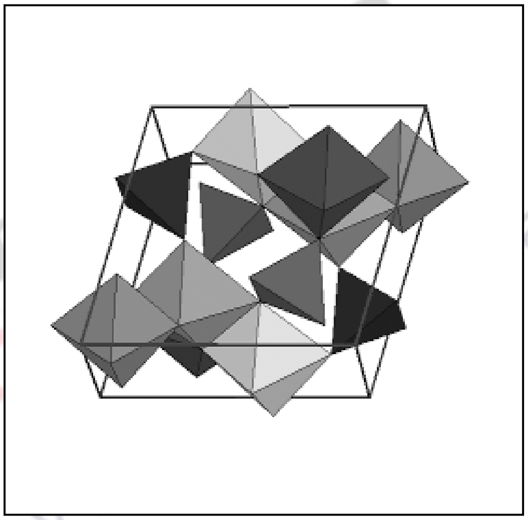

Fig. 1 Articulation of AlO_6 octahdera and SiO_4 terahedra in a-b plane of Kyanite.

Kyanite has a relatively pure $AlAlOSiO_4$ composition. Minor substitution of Fe^{3+} and Cr^{3+} can be accommodated by the kyanite structure. The small amount of Ti^{4+} substitution is due to frequent inclusion of rutile in kyanite.

Synthetic kyanite can be produced in lab at a 900 ºC and 10-40 kbar. The phase diagram of Al_2SiO_5 composition shows the triple point between kyanite, andalusite and sillmanite to lie at about 4.5 kilobars and 550ºC. It may invert to andalusite or sillimanite by a change in the pressure or temperature conditions. Kyanite also gets converted to mullite and glass on heating to ca. 1300 ºC.

Kyanite may alter to sericite, margarite or pyrophyllite. The kyanite of regional metamorphism may be involved in number of metamorphic reactions and may show reaction textures with minerals like andalusite, sillimanite, staurolite, garnet and cordierite.

3.2 Andalusite –discovered in Andalusia, Spain.

It has chains of edge sharing Al-O octahedral groups parallel to c- axis. Lateral linkage between the octahedra is provided by Si between four tetrahedrally arranged oxygen atoms alternating with Al between five oxygen atoms **(Fig.2).**

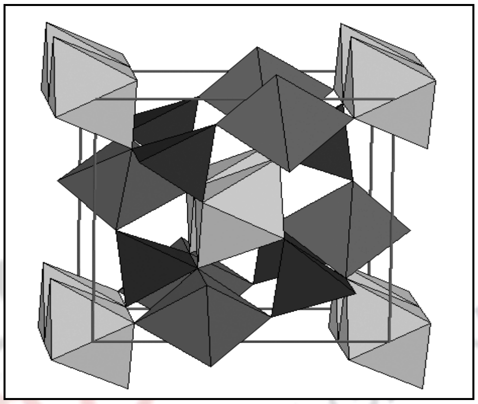

Fig. 2 Arrangement of SiO_4 tetrahdra and AlO_6 octahedra in Andalusite a-b plane.

The mineral is relatively pure $AlAlOSiO_4$ and shows substitution of Mn^{3+} and Fe^{3+} for octahedral aluminium. Extensive solid solution to *Kanonaite* is reported for andalusite with 32.2 percent Mn_2O_3 leading to a composition $(Mn^{3+},Al)AlSiO_5$. The term *Viridine* has been used for andalusite containing 4-8 percent Fe_2O_3 and 19.6 percent Mn_2O_3.

Andalusite can be synthesized from kaolinite or from a mixture of $Al_2O_3 + SiO_2$ at temperatures 450-650ºC and water vapour pressure between 0.6-2 Kbar.

Alteration to sericite, chlorite and other sheet silicates is commonly exhibited by andalusite. It also shows metamorphic reaction relations with minerals such as cordierite, staurolite, garnet, sillimanite and kyanite.

3.3 Sillimanite-after Benjamin Silliman (1779-1864) American chemist and mineralogist.

The structure of sillimanite consists of edge sharing octahedra of Al-O parallel to c –axis. Double chain of terahedra containing Si and Al alternately in 4 fold coordination provides the lateral linkage between octahedral chains (**Fig. 3**).

The composition of sillimanite is relatively pure Al_2SiO_5. Fe^{3+} and Cr^{3+} may replace the Al in the structure. Minor amount of absorbed and entrapped water is found to be present in the fibrous fibrolite variety of sillimanite.

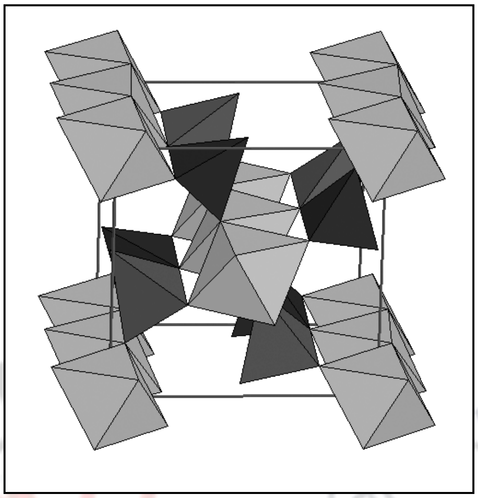

Fig. 3 Structure of Sillimanite in a-b plane

It can be synthesized from its component oxides at high pressure and temperature condition. The triple point between kyanite, sillimanite, andalusite lies at about 500 $\pm$ 50ºC and 4 $\pm$ 0.5kbar. At temperatures higher than 1000ºC it is known to convert to mullite + quartz.

It is known to be involved in many metamorphic reactions hence reaction textures with associated minerals are commonly exhibited by it. Alteration product mostly includes muscovite, sericite, pyrophyllite, kaolinite and montmorillonite.

4. Crystallographic properties

	Sillimanite	**Andalusite**	**Kyanite**
Formula weight	162.05	162.05	162.05
α	1.710-1.718	1.633-1.642	1.653-1.661
β	1.719-1.724	1.639-1.644	1.657-1.662
γ	1.724-1.734	1.644-1.650	1.672-1.683
Z	4	4	4
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Point Group	mmm	mmm	-1

Space Group	Pbnm	Pnnm	P -1
Unit Cell			
a(Å)	7.4883	7.7980	7.1262
b(Å)	7.6808	7.9031	7.8520
c(Å)	5.7774	5.5566	5.5747
Vol(Å^3)	332.29	342.44	293.72
Molar Vol	50.035	51.564	44.227
Density	3.2386	3.1426	3.6640

5. Physical properties

5.1 Kyanite in hand specimen

It commonly forms columnar or bladed elongated crystals. It has a patchy blue, grey or white and rarely light green colour (**Fig. 4**). Vitreous to pearly in lusture and gives a white streak. It has a hardness of 4-5 parallel to c direction and ~7$^{1/2}$ at right angles to c crystallographic direction. Specific gravity ranges from 3.53-3.67. Cleavage is perfect on {100}. Cleavage fragments are usually splintery. Splintery fractures are common and crystals are of brittle nature. A basal parting is conspicuous on {001} cutting at about 85º to the length of crystals. Twinning is not obvious in hand sample though single and multiple twins with {100} composition planes are common.

Fig. 4. Kyanite bearing schist of regional metamorphic terrain.

5.2 Andalusite in hand specimen

Andalusite crystals are commonly elongate prisms with a nearly square cross section. A variety called Chiastolite known to display carbonaceous inclusions along the diagonals of the prism. It can also occur as anhedral grains and irregular masses. Mostly are pink, white or pinkish brown in colour. Usually gives a hardness of 6 – 8 and specific gravity of 3.13-3.16. Vitreous in lusture and gives a white streak. {110} prismatic cleavages are observed parallel to prism faces in cross sections though may not be evident in hand samples. Subconchoidal and uneven fractures are common and crystals are of brittle nature. Twinning on {101} composition plane is rare.

5.3 Sillimanite in hand specimen

Sillimanite usually forms fibrous or slender prismatic grains. Color wise the crystals are either colourless or white. Vitreous in luster and gives white streak. It has hardness in the range of 6-8. Specific gravity ranges from 3.23-3.27. Sillimanite exhibits a good cleavage {010} parallel to length of crystals. Crystals are brittle in nature and may show uneven fracture. No twinning is reported for sillimanite.

6. Optical properties

Under plane polarized light

Kyanite It shows high relief, are commonly bladed in habit, radiating aggregates of blades are also common **(Fig. 5 left)**. Usually colourless in thin sections but may sometimes show pale blue colour. Display weak pleochroism X<Y<Z: X = colourless, Y = light violet blue, Z = light cobalt blue. Cleavage {110} perfect

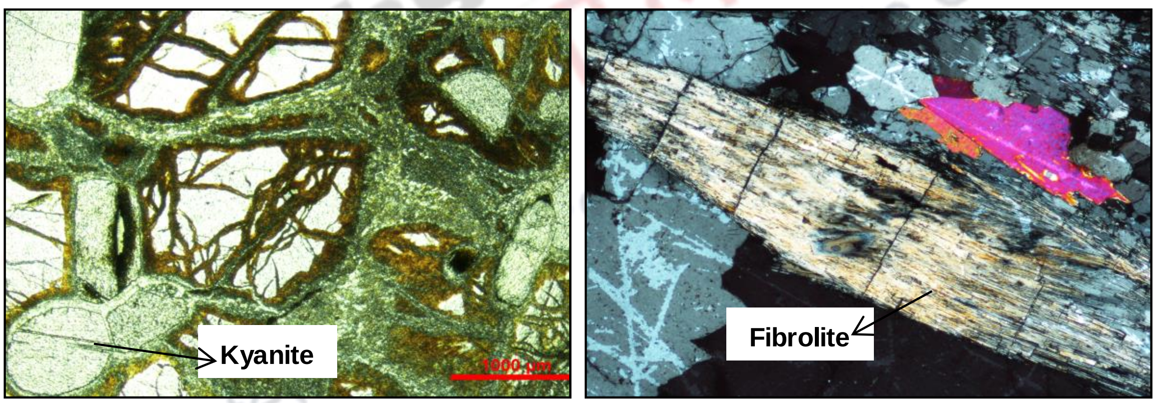

Fig. 5 (Left) Kyanite in eclogite mantle xenoliths of Wajrakarur Kimberlite field, Andhra Pradesh , India (PPL image, 5X); (Right). Fibrolite grain (golden brown) as seen in a Sillimanite bearing Schist from Arunachal Himalyas. (CPL image, 5X)

Andlusite It shows moderately high positive relief and is commonly euhedral elongate prism. Usually colourless in thin section. Exhibits weak pleochroism X= reddish pink, Y=Z= greenish yellow, Cleavage {110} good.

Sillimanite It shows moderately high relief and is usually colourless in thin section though fibrolite masses can exhibit a pale brown colour **(Fig. 5 Right)**. Most sillimanite in thin section is not visibly pleochroic. Cleavage {010} is perfect on basal section of sillimanite

Under cross polarized light

Kyanite It is anisotropic in nature, shows low birefringence, shows first order grey polarization colours, shows oblique extinction on cleavage and prism edge, are biaxial negative. Optic orientation Z ^ c and Y ^ b are both about 27-30 º and X ^ a is only few degrees, optic axial plane is nearly normal to {100}, $2V_{\alpha}$ = 73-86º, sign of elongation is length slow positive elongation **(Fig. 6)**.

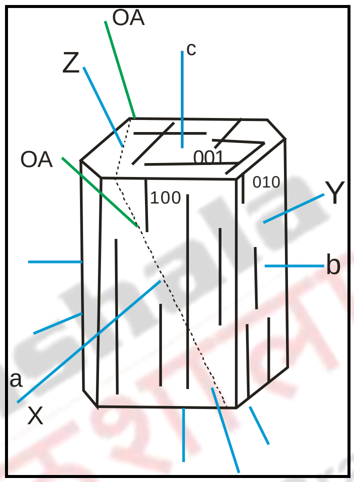

Fig. 6 Optic orientation of kyanite

Andalusite It is anisotropic in nature with a low birefringence, shows first order grey polarization colours, straight extinction on prism edge or on cleavage trace, basal section shows symmetrical extinction, are biaxial negative. Optic orientation X = c, Y = b, Z = a, optic plane is (010) for all composition ranges, $2V_{\alpha}$ = 73-82º, sign of elongation negative length fast **(Fig. 7)**.

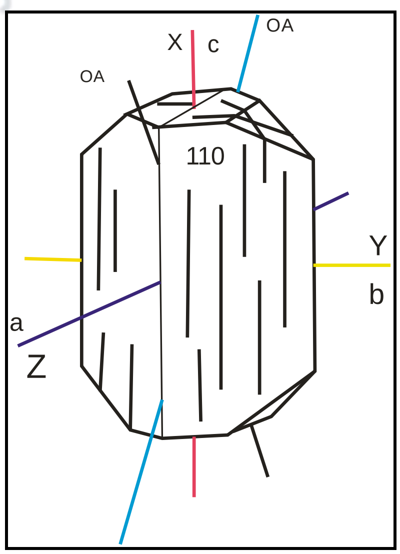

Fig.7 Optic orientation of Andalusite

Sillimanite It is anistropic in nature, shows moderate birefringence, high first order to low second order polarization colours, straight extinction on single cleavage trace and are biaxial positive. Optic orientation α = x, β = y, γ = z, optic axial plane is (010), $2V_{\gamma}$ = 21-30º, Sign of elongation is length slow positive elongation **(Fig. 8).**

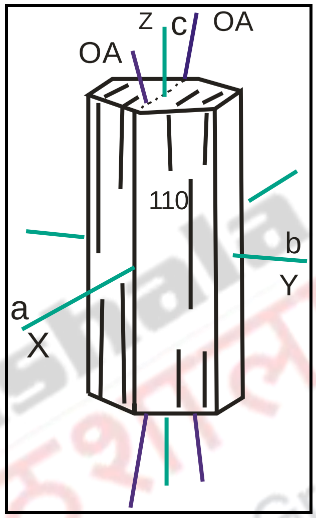

Fig. 8 Optic orientation of Sillimanite

7. Occurence

Each polymorph is known to have a specific pressure- temperature range over which it is stable with andalusite being the low pressure polymorph, kyanite stable at high pressures and sillimanite is stable at high temperatures. So, these minerals have found extensive application in establishing the pressure –temperature conditions of rocks bearing them. The stability fields of these minerals are related by phase diagram (**Fig. 9**) Being a very important mineral in metamorphic petrology the P-T stability of the aluminium silicates has been extensively studied. However problems with establishing the P-T field for these polymorphs include Al-Si order- disorder in sillimanite and small compositional variations of the minerals. It has been shown that small amounts of Fe and /or Mn entering the structure of andalusite may significantly effect its stability conditions.

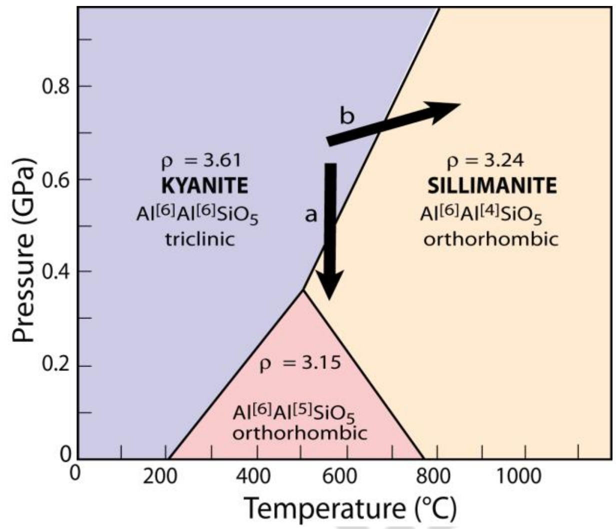

Fig. 9 Phase diagram for the Al_2SiO_5 polymorphs. The arrows show that kyanite will react to form sillimanite with increasing temperature or with decreasing pressure. Although not labeled, the pink triangular field at the bottom is the stability field for andalusite. (Source: http://serc.carleton.edu)

The alumino-silicate polymorphs kyanite, sillimanite and andalusite are characteristic minerals of medium to high grade pelitic metamorphic rocks like mica schist, biotite gneiss and hornfels. Andalusite is commonly found in contact metamorphic aureoles of shallow and intermediate depth intrusive and also in rocks subjected to medium grade metamorphism at relatively low pressures. Sillimanite is restricted to rocks that are subjected to higher temperatures and kyanite is characteristic of rocks subjected to relatively high pressures. Based on the bulk composition of the rock and grade of metamorphism underwent by a rock; these polymorphs may be found associated with cordierite, staurolite, garnet, chlorite, muscovite, biotite, plagioclase, k-feldspar and chloritoid. Eclogites an ultra high-pressure metamorphic rock are also known to contain kyanite in association with pyrope rich garnet and omphacite pyroxene.

These polymorphs are not stable in a weathering environment even tough may occur as important detrital minerals.

These polymorphs are less commonly also being reported from granites and granitic pegmatites. It's debatable whether they are primary magmatic minerals or product of post magmatic crystallization or are xenocrysts. Xenocrysts may originate from partially assimilated metamorphic wall rock or could be relicts of the rocks from which the magma was derived by partial melting. There exists no compelling evidence as to why these minerals cannot crystallize from magma of appropriate composition under appropriate pressure –temperature conditions. However one should be evaluate each case based on field textural and related chemical evidences thoroughly.

8. Use

On heating the aluminium silicates to high temperatures it gets converted to Mullite [Al ($Al_{1-2x}Si_{1-2x}$) O_{5-x}] plus quartz. Mulite is used as a refractory mineral. Mutilised aluminium silicates find use in manufacture of refractory materials such as high alumina bricks and related products used to line blast furnaces and kilns and in applications requiring resistance to temperature. Andalusite also finds use in manufacture of ceramic products, abrasives and filler materials.

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