
INTRODUCTION TO MINERALOGY

Aims: These notes describe the basic principles of mineral chemistry and structure. Some basic terms essential to understanding mineral chemistry are highlighted by **bold type face**. At the beginning of each section is a list of assumed vocabulary. You should already know the meaning of these words or, at very least, find out the meaning before the lectures commence.

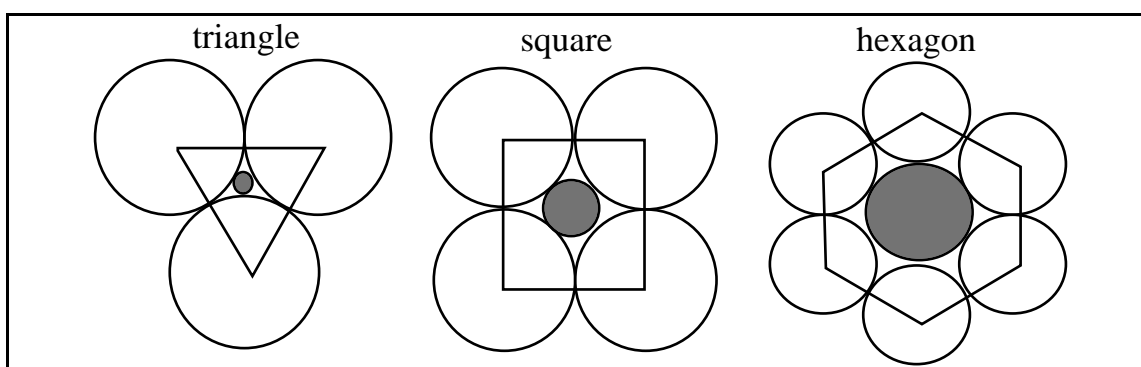
SECTION 1 : Structure and chemistry of the silicates

Required Vocabulary: ion, cation, anion, ionic compound, valency.

We begin by considering some of the principles that determine what is possible (and what is not) in the way of composition and structure in the silicates. In order to do this we need to understand the concepts of **coordination** and **charge balance** (or electrical stability);

1.1 Coordination

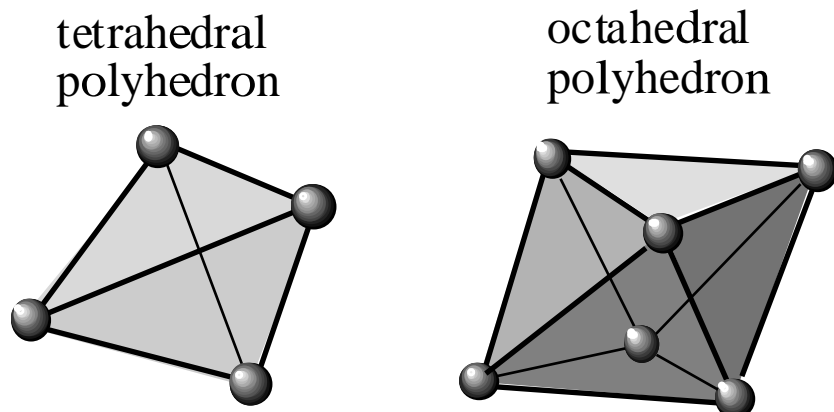
A critical concept in understanding silicate mineral chemistry (and structure) is that of **coordination polyhedra**. In order to preserve local electronic neutrality in the silicate structure, the (normally smaller) metal cations are surrounded by oxygen anions. The geometric shape formed by the bounding oxygens defines the various coordination polyhedra. In a hypothetical 2-dimensional structure we can illustrate the notion of the coordination polyhedra using various regular polygons.



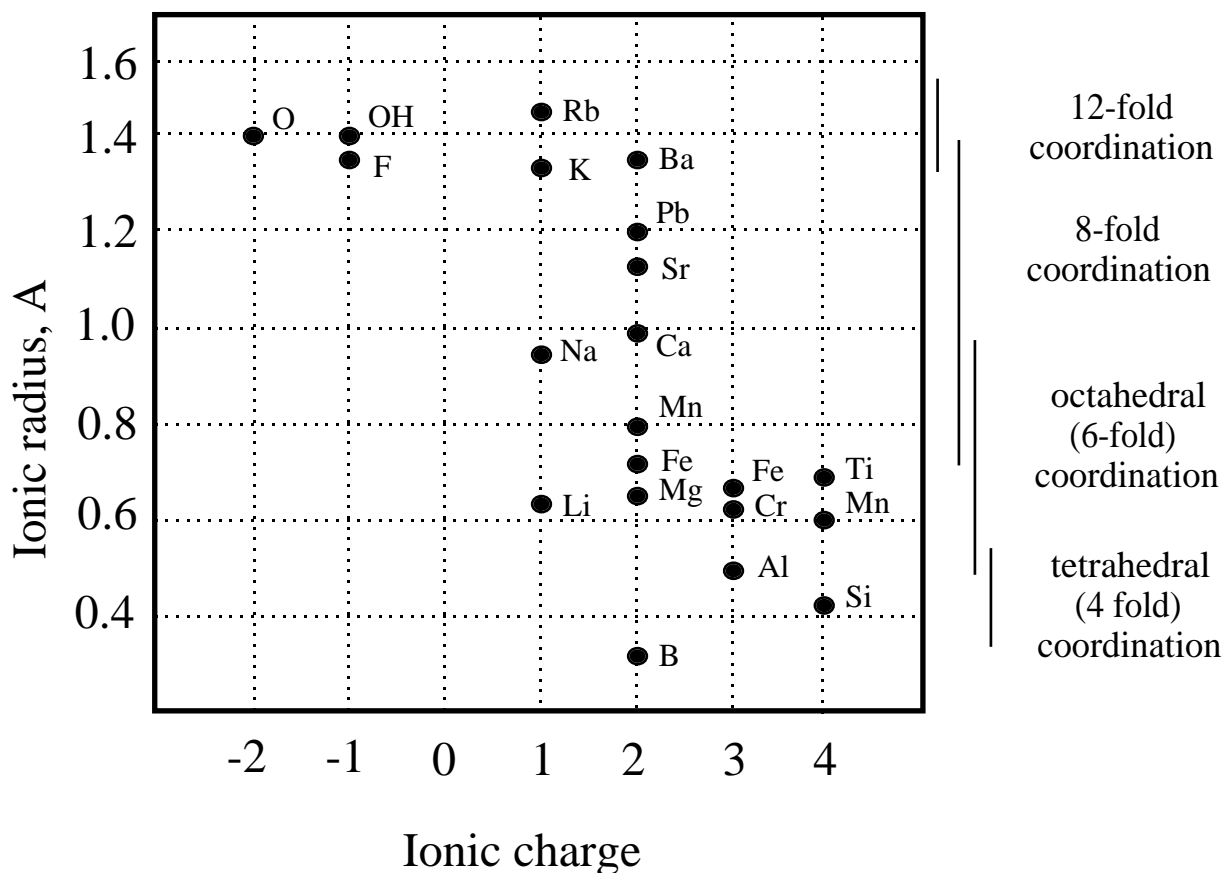
In naturally occurring 3-D silicate structures the main coordination polyhedra are **tetrahedral** or **4-fold** (with four bounding oxygens), **octahedral** or **6-fold** (with six bounding oxygens), **cubic** or **8-fold** (with eight bounding oxygens) and **12-fold**. The shape of the polyhedra formed by a particular cation is defined the relative size (as reflected in their radii) of the metal cations and the bounding anions (in our 2-D example the hexagon clearly allows a bigger relative central “atom” than the triangle).

The oxygen ion is so large in comparison to most cations that in silicate minerals the structure is dictated by the packing of oxygen ions with cations in the interstices (the Figure below shows the relationship between ionic radius and ionic charge for the common rock forming elements). In silicates, which can be considered as ionic structures, each ion tends

to surround itself with ions of opposite charge. The number of anions, say of oxygen, that can be grouped around a cation depends on the **radius ratio** of the two ions (defined as $R_{\text{cation}}/R_{\text{anion}}$) and is termed the coordination number of the cation.



With oxygen as the principal anion, as is the general case for silicates, many cations occur exclusively in one coordination. Cations that have radius ratios near the theoretical boundary between types of coordination may occur in both. Thus Al may occur in either octahedral (6-fold) or tetrahedral coordination (4), while Si occurs almost exclusively in tetrahedral coordination (4) (the only exception being in a few very high pressure and exceptionally rare phases such as the SiO_2 polymorph, *stishovite*, where Si is found in octahedral coordination).



Radius ratio ($R_{\text{cation}}/R_{\text{anion}}$)	Arrangement of anions around cation	Coordination Number of cation
0.15-0.22	corners of an equilateral triangle	3
0.22-0.41	corners of tetrahedron	4
0.41-0.73	corners of an octahedron	6
0.73-1	corners of cube	8
1	corners of an icosahedron (close packing)	12

1.2 Charge balance (or electrical stability)

The requirement for charge balance or electrical stability in silicate and other ionic compounds means that the sum of positive and negative charges on the ions must balance. This is not achieved by pairing of individual cations and anions; but rather the positive charge on a cation is divided equally by the surrounding anions, the number of which is determined by the relative sizes of the ions (i.e., the coordination number of the cation). This is summarised in one of Pauling's rules " in a stable structure the total strength of valency bonds which reach an anion from all the neighbouring cations is equal to the charge on the anion".

1.3 The structure of silicates

Since Si invariably occurs in tetrahedral coordination the fundamental unit of the silicate structure is the Si-O tetrahedra. The different types of silicate structure arise from the ways in which these tetrahedra are arranged: they may exist as separate unlinked entities, as linked finite arrays, as infinite 1-dimensional chains, as infinite 2-dimensional sheets or as infinite 3-dimensional frameworks. These possibilities give rise to the six primary structural types of silicates, each with a characteristic Si : O ratio (more strictly this should be the ratio of tetrahedral cations to oxygen, the reasons for which are discussed later):

Orthosilicates (or neosilicates): independent Si-O tetrahedra, Si : O = 1 : 4, for example the *olivine* group.

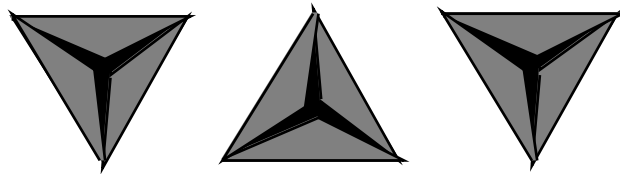
Sorosilicates : two linked Si-O tetrahedra sharing one oxygen, Si : O = 2 : 7

Cyclosilicates : closed rings of linked Si-O tetrahedra sharing two oxygens, Si : O = 1 : 3, for example *beryl*.

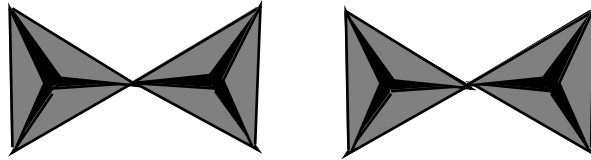
Inosilicates : continuous chains of Si-O tetrahedra, sharing two oxygens (single chains, Si : O = 1 : 3, for example the *pyroxene* group) or alternately sharing two and three oxygens (double chains, Si : O = 4 : 11, for example the *amphibole* group)

Phyllosilicates: Continuous sheets of Si-O tetrahedra sharing three oxygens, Si : O = 2 : 5, for example the *mica* group.

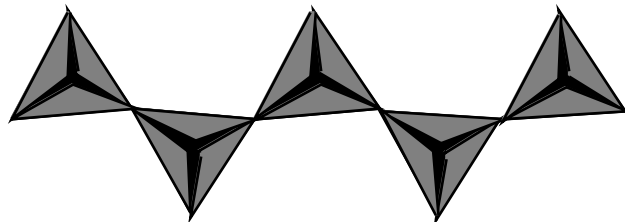
Tektosilicates: Continuous framework of Si-O tetrahedra sharing all four oxygens, Si : O = 1 : 2, for example the *feldspar* group.



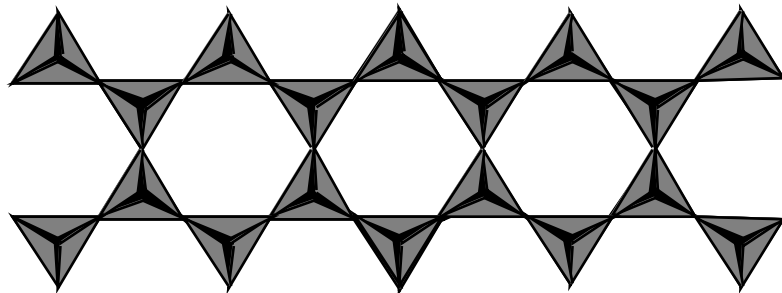
orthosilicate



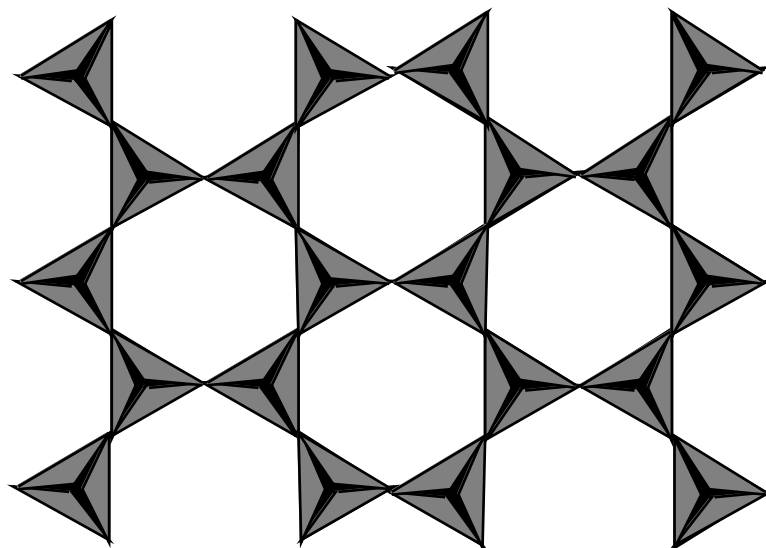
sorosilicate



single chain inosilicate

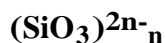


double chain inosilicate

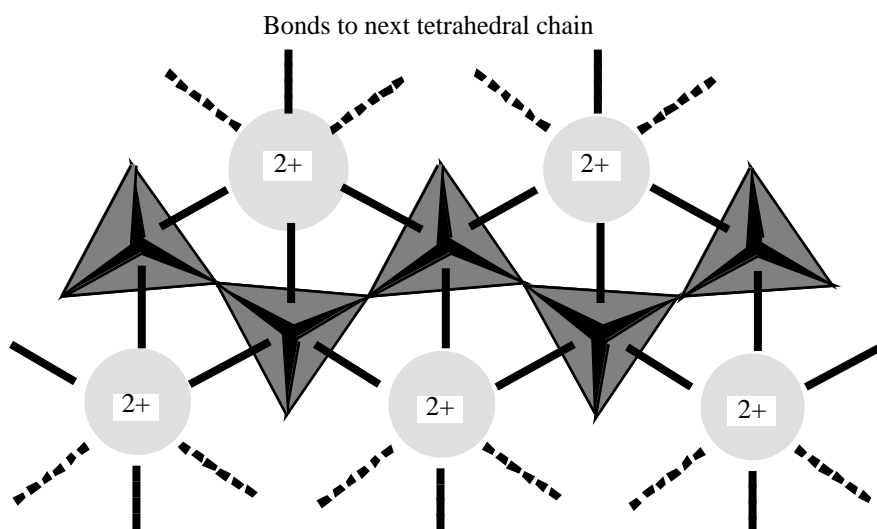


phyllosilicate

The requirement for charge balance or electronic neutrality in these different structural types is maintained by the dispersal of other cations in 6-fold (octahedral), 8-fold (cubic) or 12-fold (icosahedral or close packed) coordination between the individual tetrahedra or arrays of tetrahedra in the silicate structure. For example, in single chained inosilicates (Si : O = 1 : 3) there is a net excess of two negative charges per tetrahedra.

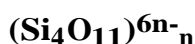


where n is the number of tetrahedra in the chain, and $2n^-$ represents the charge excess of the chain forming elements. Theoretically the charge excess could be alleviated in a number of different ways, for example by adding one bivalent cation or two univalent cations per 3 oxygens. However, the location of these cations, which must reside in spaces (termed sites) between the individual chains of Si-O tetrahedra, must be such that they simultaneously satisfy the requirement for electronic neutrality of all oxygens in the structure. Fortunately, this constraint severely limits the range of compositions and structures found in the inosilicates (as indeed it does with all other silicates).

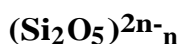


If we look at the detail of the single chain structure we find that in each tetrahedron there are two linking O atoms that are each bonded to two Si atoms and two peripheral O atoms each with bonds to only one Si atom. Since each Si atom shares its 4^+ charge with the surrounding four oxygens of the tetrahedron, the requirement for the electronic neutrality for each of the two linking O atoms is completely satisfied. In contrast, each of the peripheral O atoms have a net excess of one negative charge. In order to satisfy this each of these oxygens can be bonded with 3 neighbouring bivalent cations in octahedral coordination (as shown above) or with four bivalent cations in 8-fold coordination. In the *pyroxene* group both possibilities occur, each placing profound constraints on the way in which the adjacent chains are located with respect to each other.

In double chain inosilicates (Si : O = 4 : 11) the chain forming elements give rise to the basic formula:



where the net excess of charges per 11 oxygens is equivalent to 6 negative charges. The sheet forming elements in phyllosilicates (Si : O = 2 : 5) give rise to the basic formula:



SECTION 2: Chemical substitutions and the notion of compositional space

2.1 Chemical substitutions

The principles of coordination and charge balance limit the possible structures of the silicates, and therefore constrain the total range of possible compositions found in natural minerals. The fact that many cations have similar sizes allows for a large range of chemical substitutions in the silicates. For instance Fe^{2+} and Mg have a similar size and identical valency. Their similar size implies that they have the same coordination number (6) and thus they are able to fit in the same crystallographic sites, while their identical valency implies that the substitution does not violate the electronic stability of the structure. We find therefore that many naturally occurring silicates show a complete range in substitution of Fe and Mg (for example, in the pyroxene, amphibole and mica groups). The substitution of Fe for Mg on a octahedral site can be written conveniently :



where vi refers to the cations located on a octahedrally (6-fold) coordinated site.

Aluminium plays an important role in silicates since apart from Si it is the only common cation which can exist in tetrahedral coordination. It is therefore able to substitute for Si. However, since Al is trivalent while Si is quadrivalent this substitution violates the charge balance requirement and thus cannot therefore occur by itself. However it can occur if it is coupled with another substitution on a nearby crystallographic site which preserves charge balance. For instance the substitution of a tetrahedral Al (written Al^{iv}) for Si^{iv} :



could be coupled with the substitution of octahedral Al for Fe^{vi} or Mg^{vi} :



The complete coupled substitution can then be written :



Note that this is a valid substitution since it is charge balanced. *All valid substitutions must be charge balanced.*

The role of Al^{iv} substitution is particularly important in the tectosilicate *feldspar* group. Feldspars consist of 3-dimensional frameworks of linked Si-O and Al-O tetrahedra. The ratio of Al-O to Si-O tetrahedra in feldspars is never greater than 1 : 1 (and may be as little as 1:3) because Al-O tetrahedra tend to avoid linking to each other (the so-called Al-avoidance principle). Oxygens linking two adjacent Si-O tetrahedra are electronically neutral, while oxygens linking adjacent Si-O and Al-O tetrahedra have an excess of 1/4 of a negative charge. This excess charge cannot be balanced by Mg^{vi} or Fe^{vi} (which would contribute 1/3 of a positive charge to each linked oxygen) but can be balanced by univalent or bivalent cations with larger coordination numbers (8-fold or 12-

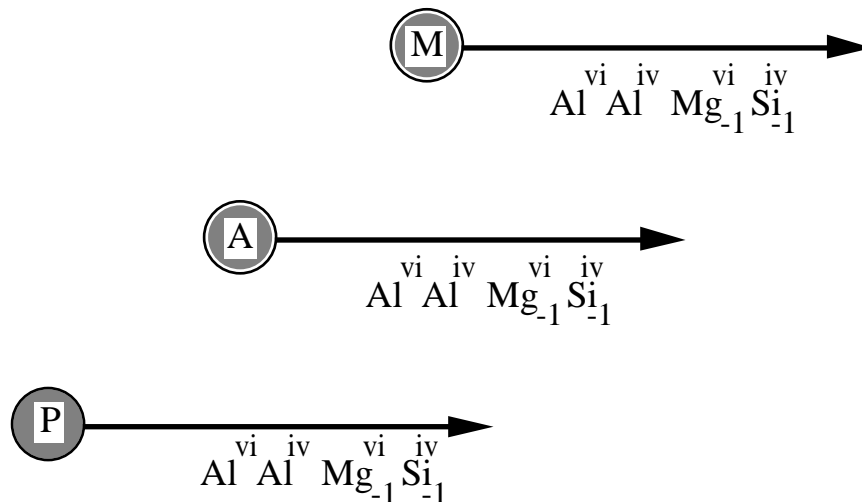
fold coordination). Cations which fit the bill include Ca, Ba, Na and K, all of which are found in naturally occurring feldspars.

2.2 The notion of compositional space

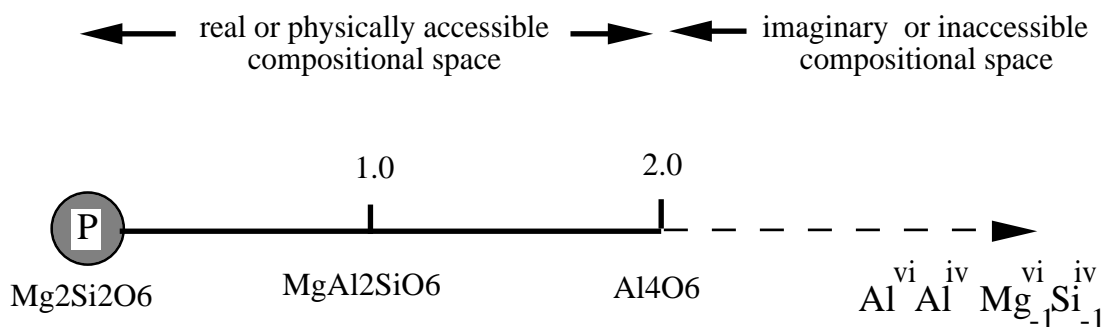
There are large number of possible substitutions in the silicate minerals. Of these only a handful are important in as much as they describe the great proportion of the compositional range of the common rock forming silicates. These important substitutions occur in a wide range of mineral groups: for example, the substitution described above:



which is so common that it is given the special name *Tschermak's substitution* is important in pyroxenes, amphiboles and micas (three of the most common rock forming mineral groups). If we designate the standard compositions (or *key component*) of the pyroxene ($\text{Mg}^{\text{vi}}_2\text{Si}^{\text{iv}}_2\text{O}_6$), amphibole ($\text{Mg}^{\text{vi}}_7\text{Si}^{\text{iv}}_8\text{O}_{22}(\text{OH})_2$) and mica ($\text{K}^{\text{xii}}_2\text{Mg}^{\text{vi}}_6\text{Al}^{\text{iv}}_2\text{Si}^{\text{iv}}_6\text{O}_{20}(\text{OH})_4$) groups by P, A and M respectively, then we can draw maps which show the compositional effect of the Tschermak substitution on each of these standard compositions:



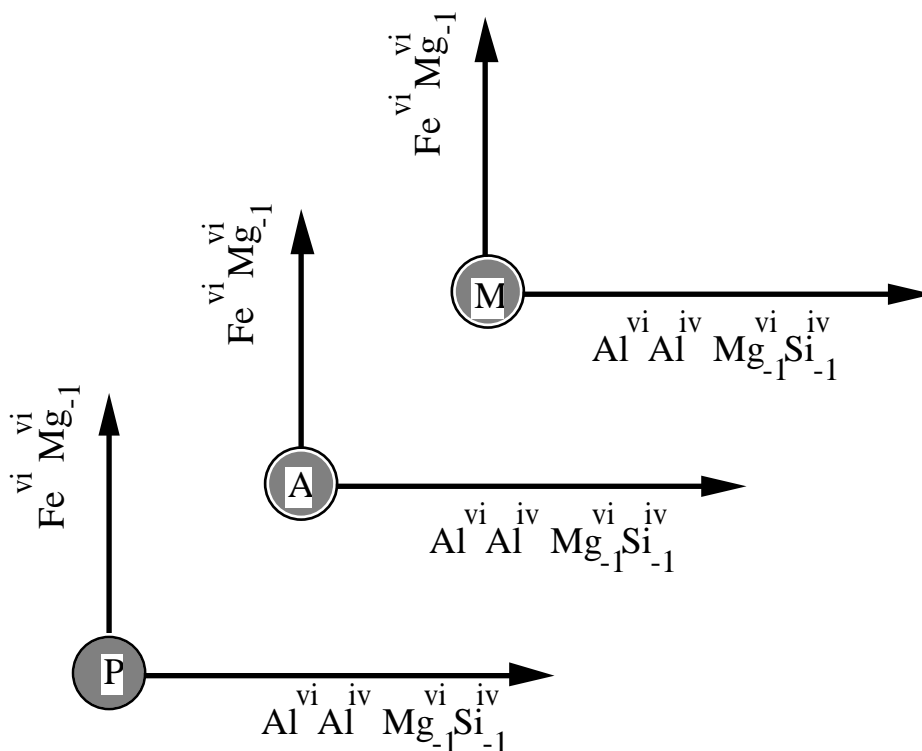
The *key* component for each group has been awarded a point in compositional space upon which the Tschermak substitution works as a vector. Clearly, the extent of possible Tschermak's substitution in any mineral group is limited by the initial composition upon which it operates. Thus we cannot perform the Tschermak substitution more than twice in real pyroxenes before we run out of Si and Mg:



(It turns out that structural constraints limit the maximum Tschermaks substitution to much less than 1.0 in natural pyroxenes). We can continue to build up our picture of compositional space by adding other common substitutions, for example:

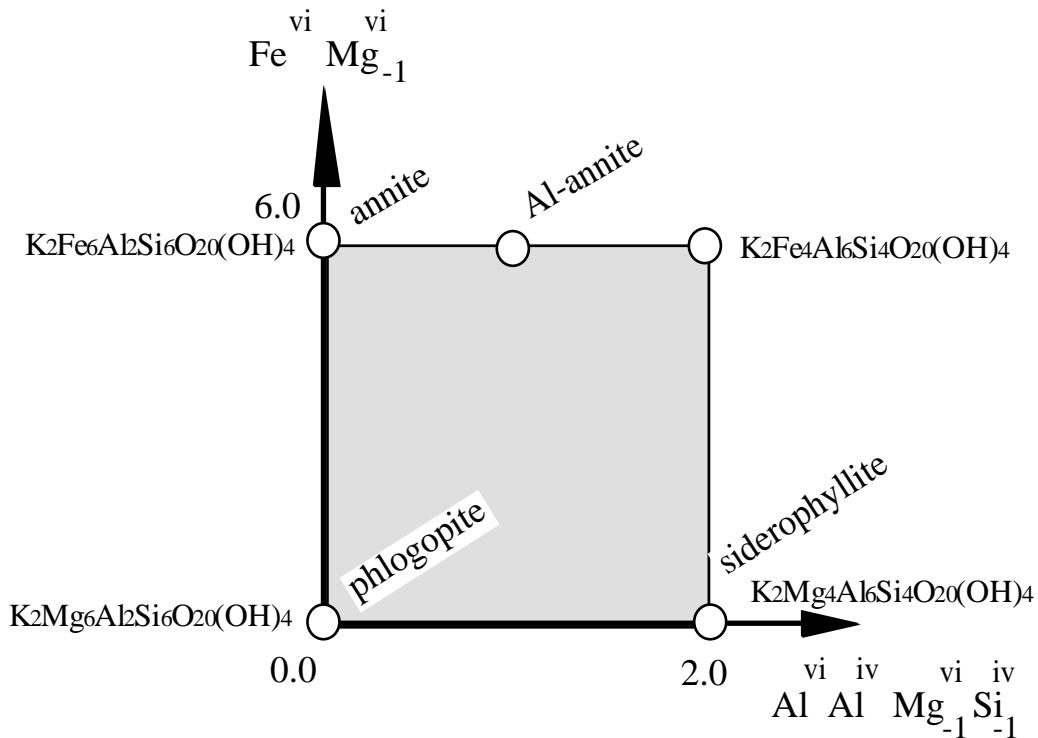


The updated maps of the compositional space for the three groups now look like this:



In these maps the axes bound a region of potential compositional variation in each of the groups. For example, the majority of common trioctahedral micas (or biotites) are defined by this exact mapping, shown below.

In reality the composition realm of many mineral groups, particularly the amphiboles, needs more than two substitutions acting on the key component. Although this is clearly difficult to draw on a 2-dimensional paper, the principles remain the same (the only difference between 3-dimensions and 4-dimensions is in our mind which is used to thinking about things in terms of geographical space. Compositional space can have many more dimensions than the 3-dimensions of our earthly geographical space). However, an important aspect of using substitutions in this way is that substitutions are common to many mineral groups, the only thing that differs is the starting composition (or *key component*) on which the substitutions operate. Moreover, a quick inspection of the starting composition should allow you, with some knowledge of the coordination number and valency of the various cations, to determine which substitutions are likely to operate in that particular group.



compositional space of the
trioctohedral mica group
(biotites)

A baffling array of mineral names have been awarded to various points in the compositional space of the compositionally complex mineral groups such as the pyroxenes, amphiboles and micas. Most of these names were awarded before there was a clear idea of the nature of the substitution mechanisms which operated in these groups, and consequently there does not seem to be much rhyme or reason to these names. In the following weeks we will introduce the names of some important points in the compositional spaces of each of these mineral groups (and expect you to remember some of them). However, more importantly we hope (by presenting mineral compositional space as a series of common substitutions which operate on a single key component) *that you will be able to predict the compositional realm of the mineral groups once you have learnt the one key component for each of the groups.*

SECTION 3 : Shape and symmetry in crystals

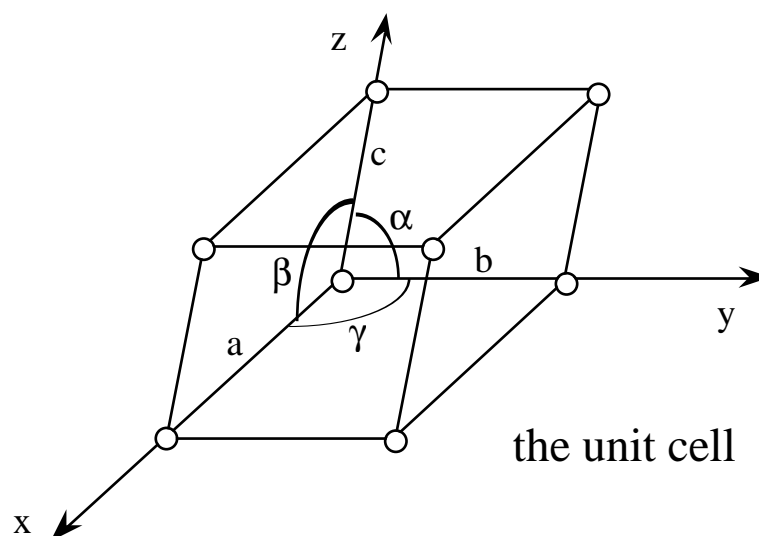
In the previous section we introduced some of the necessary mental tools needed to understand why certain minerals exist. In this section we further develop these ideas in order to understand why crystals are shaped the way they are. Ideas about shape and symmetry in crystals will be of particular benefit in understanding the optical properties of crystals that can be determined using the petrologic microscope.

3.1 The Unit Cell

We have seen that the requirement for electronic neutrality in crystals, together with coordination, provides important constraints on the arrangements of atoms within crystals. One important consequence of these constraints is that structures within individual crystals are repeated on a regular basis. For example imagine that we were sufficiently small (smaller by a factor of $\sim 10^{-11}$!) that we were able to travel along the tetrahedral chain in a single chain inosilicates such as a pyroxene. As we travelled along we would pass by an identical structural and chemical environment every two tetrahedrons. This similarity would extend to the position and coordination of the adjacent inter-chain cations as well as the distribution and orientation of the surrounding tetrahedra (one interesting consequence would be that without some independent frame of reference we could not possibly tell that we were making any headway as we travelled along the chain as we would constantly be returning to an identical and therefore indistinguishable environment). The scale of this repeat distance is astonishingly small; along the length of the tetrahedral chains in pyroxenes it is $\sim 5.3 \text{ \AA}$ (that is $5.3 * 10^{-10}$ metres).

The recognition that identical structures are repeated within crystals allows us to identify a fundamental 3 dimensional repeat unit called the **unit-cell**. The unit cell is a parallelepiped (you do know what a parallelepiped is, don't you?) with edges defined by three non-coplanar directions (these directions are defined as **x**, **y** and **z**). Importantly there is no requirement that these directions, which define the edges of the unit cell, are orthogonal (although they sometimes are); they simply define the edges of the (unit-cell) parallelepiped which has the following properties:

- (1) an infinite crystal can be made up simply by repetition of the parallelepiped along the **x**, **y** and **z** directions.

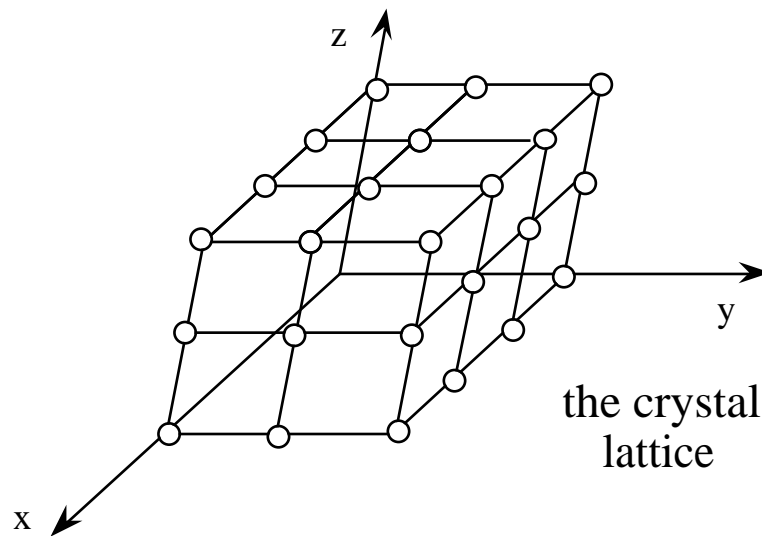


- (2) the axes and the dimensions of the edges of the parallelepiped are chosen so that the volume of the parallelepiped is the smallest possible unit which on repetition is capable of producing the structure of the infinite crystal.

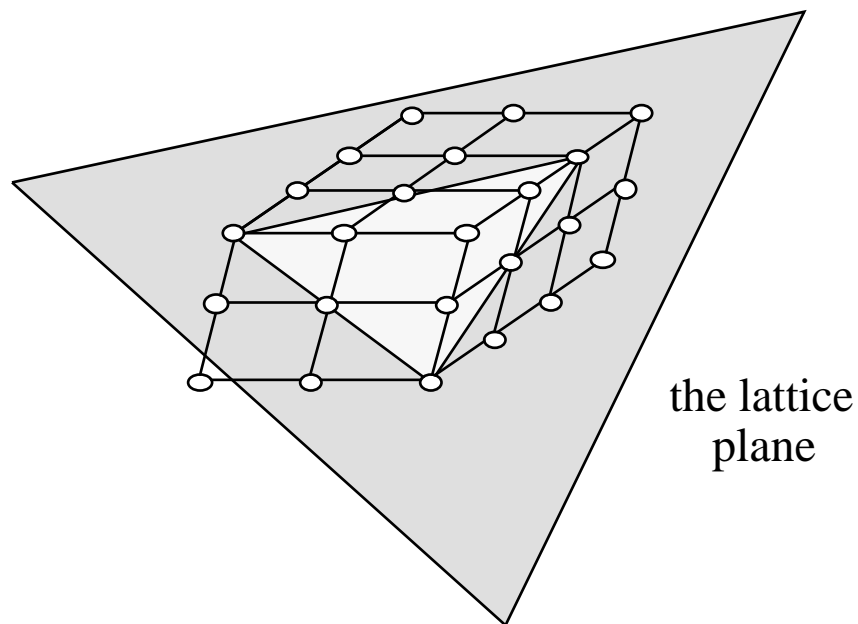
The lengths of the unit cell parallel to \mathbf{x} , \mathbf{y} , and \mathbf{z} are respectively denoted \mathbf{a} , \mathbf{b} and \mathbf{c} , and the interaxial angles $\alpha = \mathbf{y}^{\wedge}\mathbf{z}$, $\beta = \mathbf{z}^{\wedge}\mathbf{x}$ and $\gamma = \mathbf{x}^{\wedge}\mathbf{y}$.

3.2 Crystal Lattices

One of the consequences of the way in which we have defined the unit cell is that the corners of the cell have absolutely identical chemical and structural environments (in addition, in some crystals there may be locations other than at the corners of the unit cell which also have identical environments). It is useful to imagine a hypothetical crystal made up of numerous unit cells stacked along the three repeat direction, \mathbf{x} , \mathbf{y} and \mathbf{z} , with the corners of each individual cell marked by a point. These points together with any other points in the crystal with identical environments are termed *lattice points*:



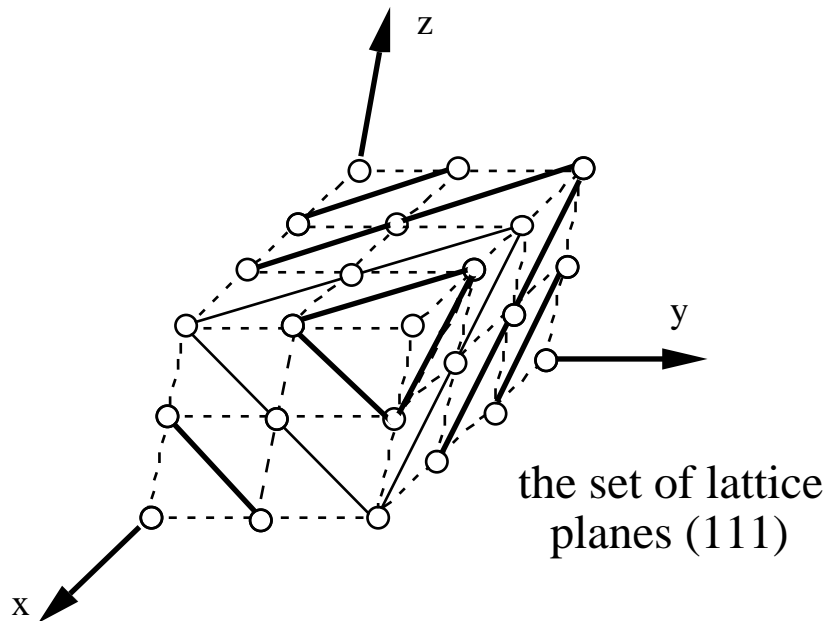
The array of lattice points is termed the *crystal lattice*, while a plane passing through three non-collinear lattice points is known as a *lattice plane*.



This notion of a crystal lattice provides a wonderful insight into many of the fundamental properties of crystals such as shape and symmetry. For example a crystal growing free of interference will tend to develop faces parallel to lattice planes, and in particular lattice planes with the greatest density of lattice points. The concept of the crystal lattice therefore provides us with a very useful way of understanding the seemingly infinite variety of crystal shapes found in nature. In order to make full use of the lattice concept we will need to (stretch the neurons in order to) develop some technique enabling the systematic description of the orientation of lattice planes and rows.

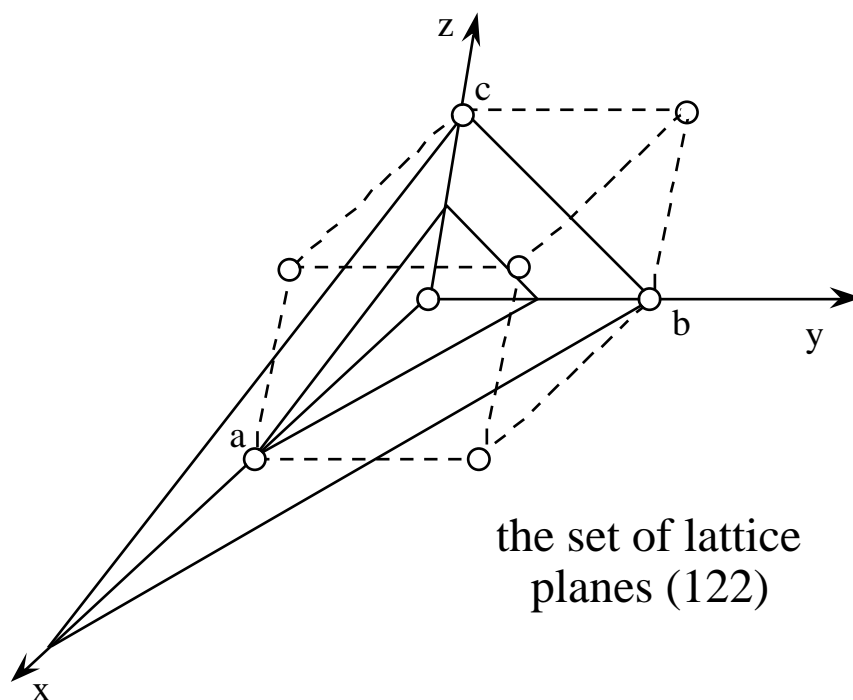
3.3 Crystallographic (Miller) indices

For a lattice plane of any orientation there will be a set of parallel planes which can be drawn such that they pass through all points other lattice points. For obvious reasons all parallel lattice planes are termed a *set of lattice planes*:



Miller indices of lattice planes:

A set of lattice planes intercept each of the crystallographic axes a finite number of times per unit length of axis. By convention, the number of intercepts of planes per unit length along the **x**-axis is termed **h**, per unit length along the **y**-axis is termed **k** and per unit length along the **z**-axis is termed **l**. The unit length along each axis is taken to be the length of the unit cell parallel to that axis, that is **a** for the **x**-axis, **b** for the **y**-axis and **c** for the **z**-axis. The *Miller Indices* of the plane are then **(hkl)**. Thus the set of lattice planes **(hkl)** divides **a** into **h** parts, **b** into **k** parts and **c** into **l** parts. An alternative way of conceptualising Miller indices is to consider the first plane out from the origin in any set of planes. This plane will make the intercepts **a/h**, **b/k**, **c/l** (where **h**, **k** and **l** are integers), on the **x**-axis, **y**-axis and **z**-axis respectively.



In some sets of lattice planes the intercepts the first plane out from the origin intercepts one or more of the axes in the negative direction along those axes. The Miller indices with respect to those axes are then written with a bar over the top of the index ($\bar{h}\bar{k}\bar{l}$) (which is read bar "h", bar "k" bar "l").

Lattice planes parallel to one of the axes will have no intercept with that axis and therefore have the Miller index of 0 with respect to that axis. Thus, in terms of Miller indices the unit-cell can be described as the parallelepiped bounded by adjacent lattice planes of the set (100), (010) and (001).

Lattice rows:

The intersection of two non-parallel lattice planes defines a *lattice row*. Such a row is indexed with reference to the parallel row passing through the origin. The indices of the line [UVW] are taken to be the coordinates of the first lattice point out from the origin through which that line passes. Note that lattice row reference indices are always enclosed in square brackets "[]" while plane reference indices are enclosed in round brackets "()".

3.4 The shape of the unit cell and the crystal systems

Fortunately, there are only seven qualitatively different shapes that a parallelepiped can adopt, and hence the unit cell of all minerals can have only seven qualitatively different shapes. These shapes give rise to seven basic crystal systems characterised by the following properties:

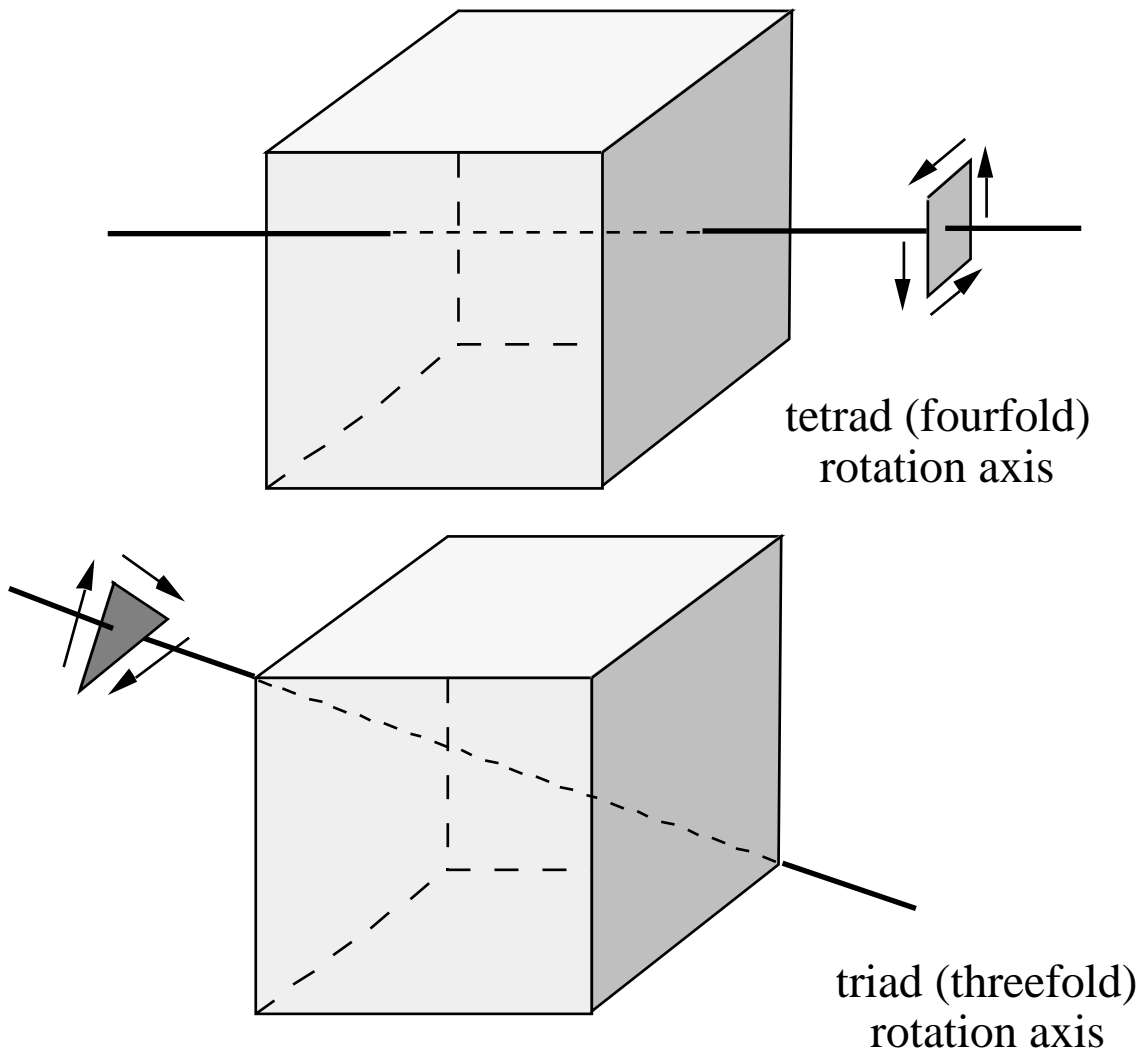
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta > 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$

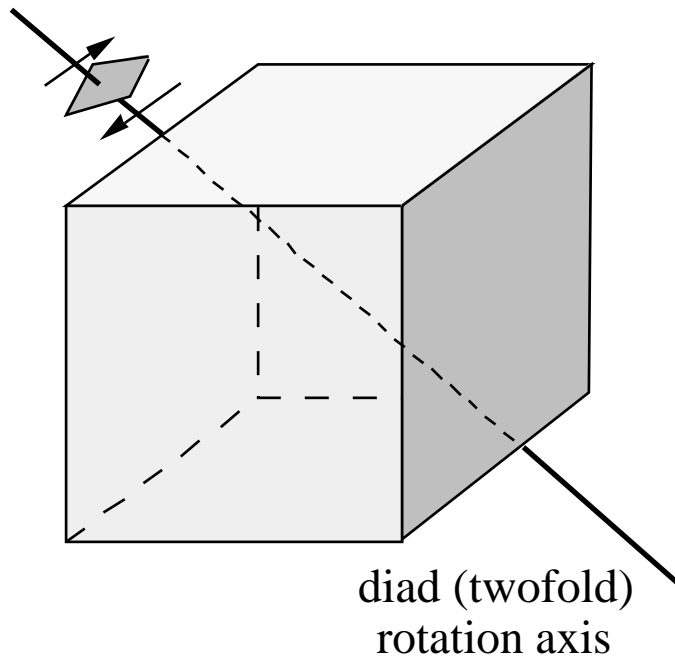
3.5 Symmetry in crystals

Each of the seven crystal systems is characterised by different symmetries. By inspection of the above table we can see that there must be a general decrease in the symmetry from the cubic system down through to the triclinic system. Consequently, the triclinic system is said to have *lower symmetry* than the cubic system and, conversely, the cubic system *higher symmetry* than the triclinic system.. In order to understand the basic symmetry elements in crystallography we will initially consider examples of the symmetry elements in a cube ($\mathbf{a} = \mathbf{b} = \mathbf{c}, \alpha = \beta = \gamma = 90^\circ$). The basic symmetry elements are:

Rotation axes of symmetry:

Rotation axes of symmetry are axes which upon rotation reproduce the exact configuration of the crystal. An n-fold rotation axis of symmetry repeats the structure n times in one complete 360° rotation. In crystals rotation axes can be sixfold (termed hexad), fourfold (tetrad), threefold (triad), twofold (diad), or onefold (monad). The monad is a trivial since it merely states that upon rotation through 360° the crystal returns to the initial position. A cube contains a number of different tetrads, triads and diads (try and determine the total number in each case):



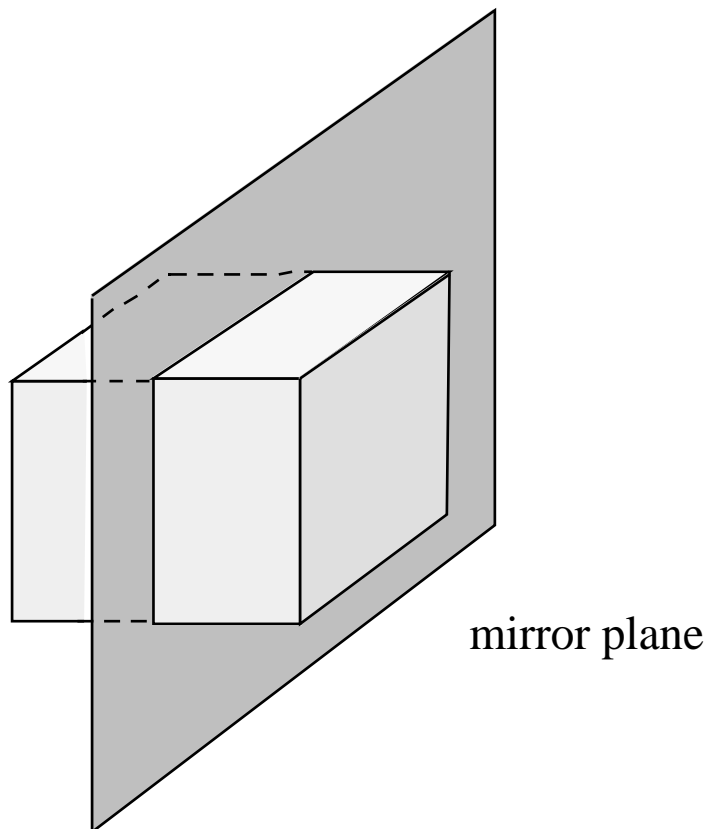


Centre of symmetry

If every atom in a crystal structure with coordinates x , y and z is duplicated by an atom at \bar{x} , \bar{y} and \bar{z} , the structure is said to possess a *centre of symmetry*.

Mirror planes:

Planes which divide crystals into mirror images are termed *mirror planes*.



Inversion axes of symmetry:

A symmetry type involving a rotation about a line plus an inversion through a point (on the line) is known as an *inversion axis of symmetry*. In any crystal the operation of an inversion axes of symmetry can always be achieved by a combination of the other symmetry operators in that crystal.

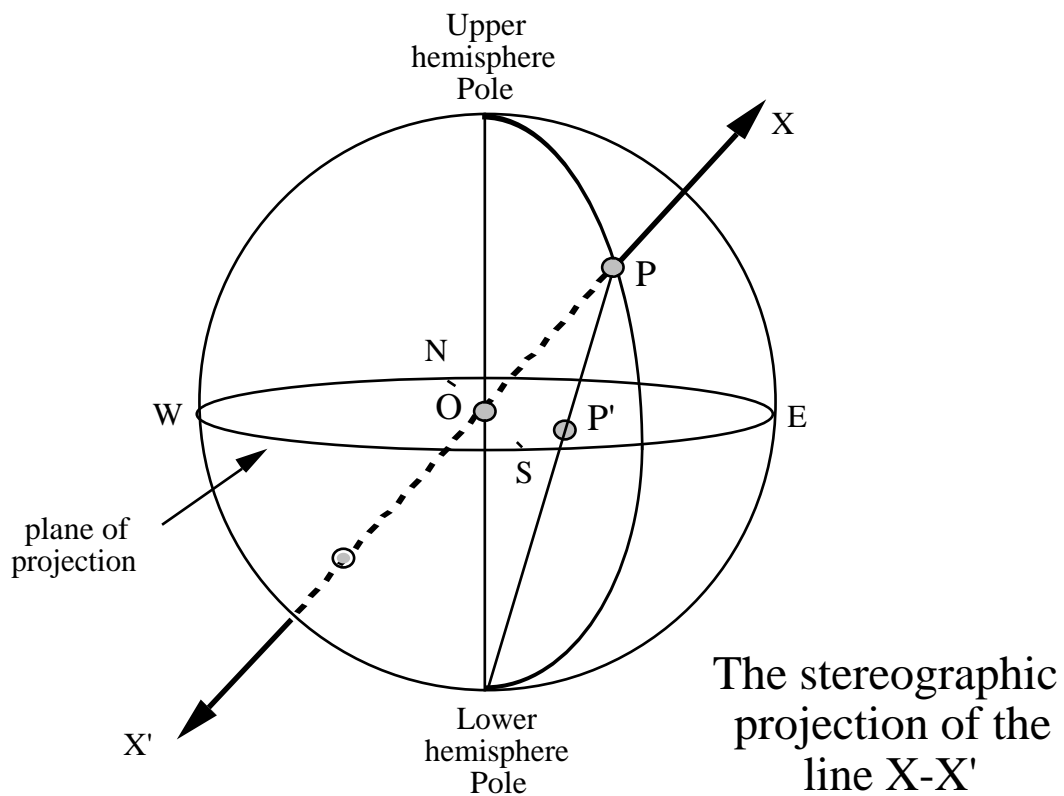
As already stated each of the seven crystal systems have characteristic symmetries. Recognition of these symmetry elements allows us to classify any crystal into the appropriate class. For example the presence of a tetrad indicates either cubic or tetragonal; more than one tetrad and it must be cubic (however, the presence of a tetrad is not the characteristic symmetry element of the cubic system which is, rather, the presence of three triads). Hexads are diagnostic of the hexagonal system, while triads preclude triclinic and monoclinic systems. The triclinic system has no rotational axes of symmetry, except of course the trivial monad. The characteristic symmetry elements in each of the seven groups are listed below:

Cubic	Three triads
Hexagonal	One hexad ($// z$)
Tetragonal	One tetrad ($// z$)
Trigonal	One triad ($// [111]$)
Orthorhombic	Three perpendicular diads ($// x, y$ and z)
Monoclinic	One diad ($// y$)
Triclinic	-

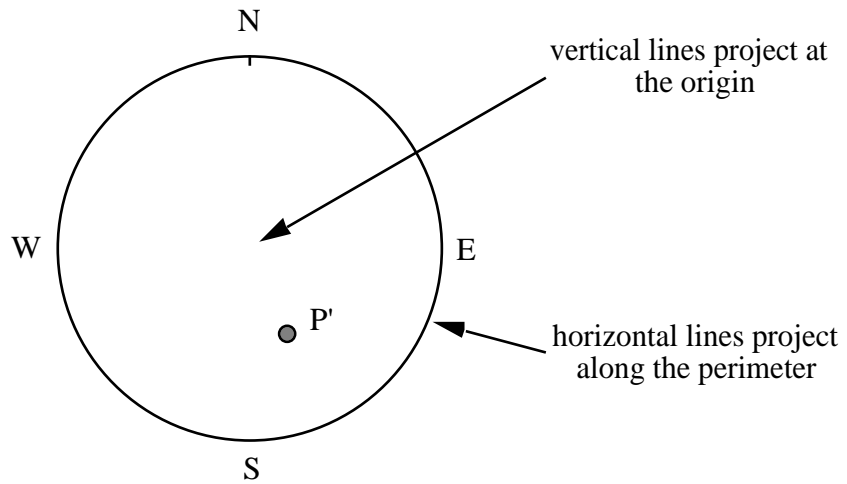
Appendix 3.1. The stereographic projection

In many texts on crystallography you will come across the stereographic projection. Because of time limitations we will probably not have a formal practical session on the stereographic projection, however the following notes are included here for the more adventurous of you who really want to come to grips with crystallography. The stereographic projection provides a useful way of conveying information about the orientation of lines and planes in 3-dimensional space (the principal problem with this being the limitations imposed by trying to portray 3-dimensional information on 2-dimensional sheets of paper).

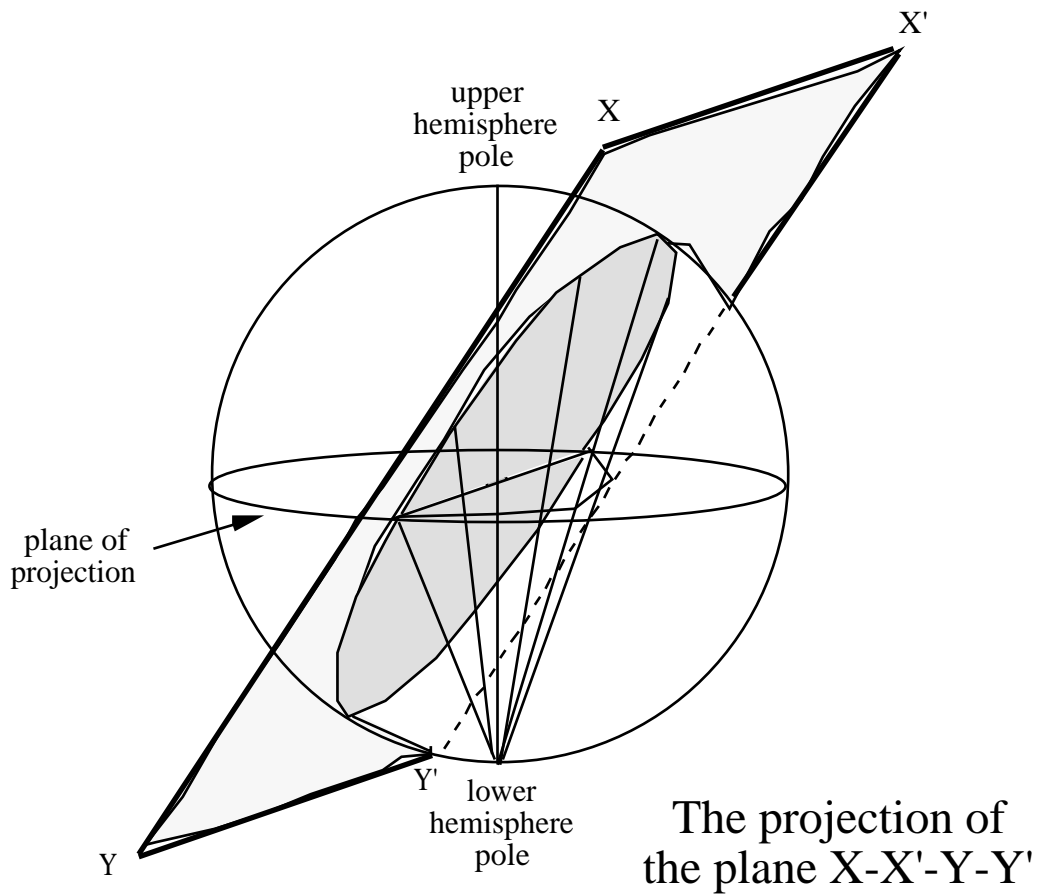
About any line $X-X'$ we can construct a sphere with its origin centred on the line. The line must intersect this sphere at two points, one in the upper hemisphere and one in the lower hemisphere (unless of course it is a horizontal line in which case it intersects the equator twice). A new line constructed from the intercept on upper hemisphere (P in the figure below) to the lower hemisphere pole, will intercept a horizontal plane passing through origin of the sphere, in a unique position (P') dependent only on the orientation of the line $X-X'$. This point P' represents the stereographic projection of the line $X-X'$.



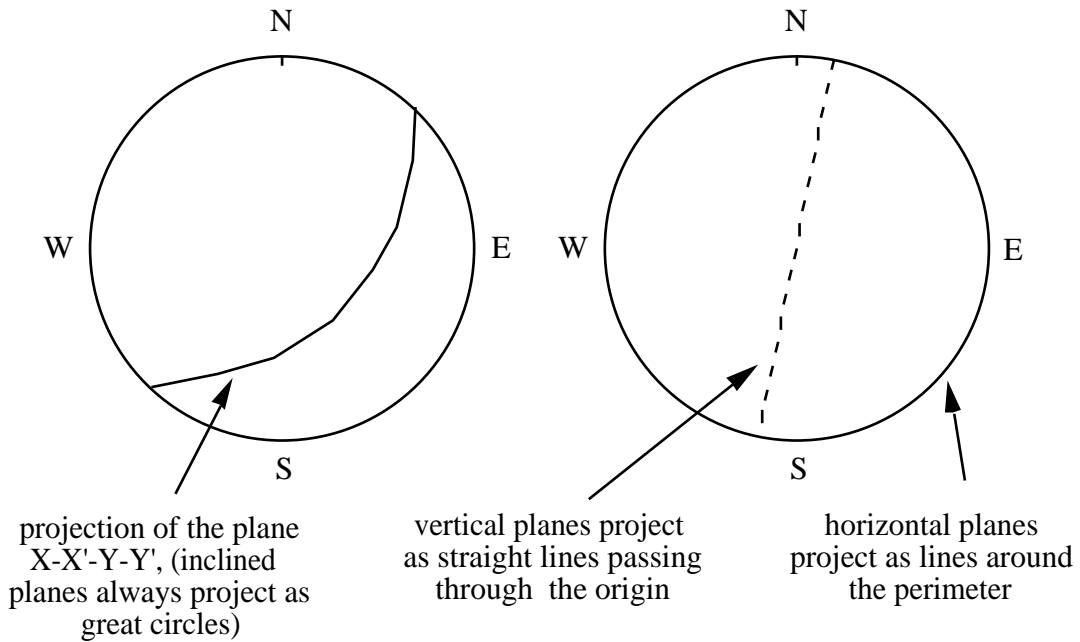
The projection plane viewed from directly above looks like this:



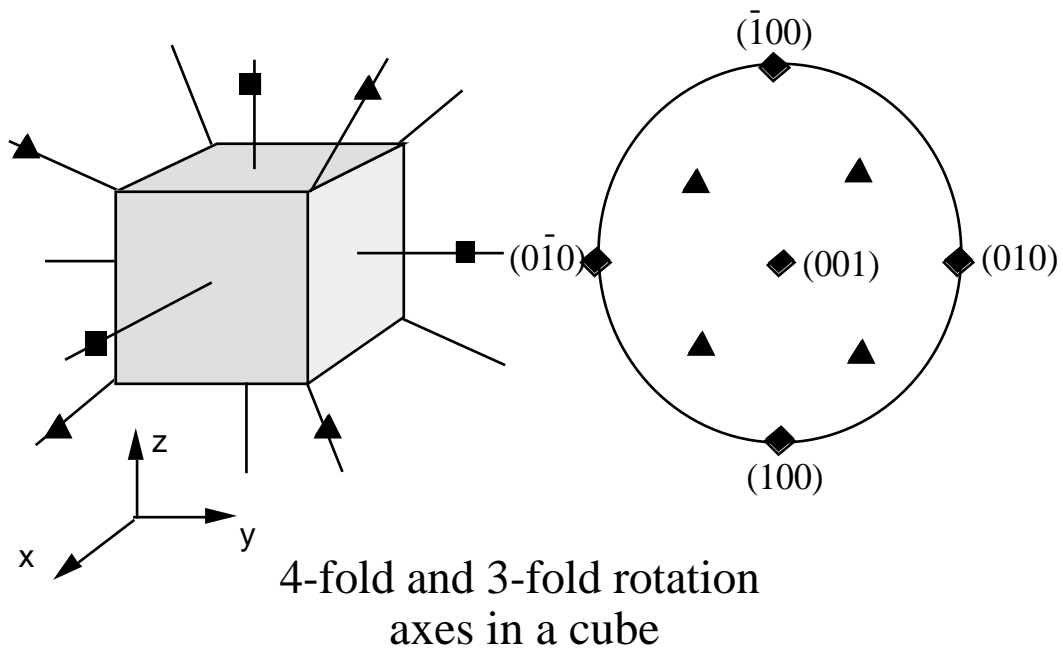
Planes can be treated in a similar fashion, although in this case the projection is a line (termed a great circle).



The projection of the plane X-X'-Y-Y' looks like this:



So far we have discussed the stereographic projection from the point of view of geographical coordinates (you will use stereographic projections based on geographical coordinate systems in structural geology, utilising a lower hemisphere projection scheme rather than the upper hemisphere projection scheme shown here). What use, you may ask, is all this in crystallography where we are largely concerned with lattice planes whose orientation is defined with respect to a coordinate set dictated by the unit-cell and which therefore is not necessarily an orthogonal coordinate set. Well, the stereographic projection provides a powerful graphic method for conveying quantitative information about the orientation of crystal faces as well as symmetry elements, for example the triads and tetrads in a cube can be illustrated in the following way (try to plot all the diads and mirror planes in the cube):



When dealing with crystal faces it is convenient to plot the orientation of the *pole* to the crystal face rather than the plane itself; the pole to a plane simply being the line perpendicular to that plane.

