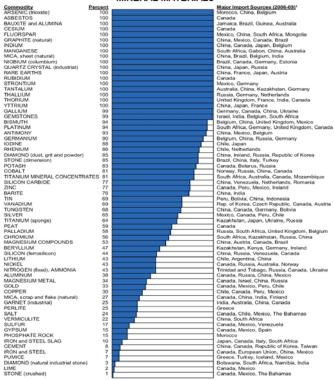
Earth Materials 114 Lecture Notes

Introduction

Read Chapters 1 & 2 of Klein & Philpotts or Read Chapter 1 of Nesse (2000)

Strategic Minerals and Metals

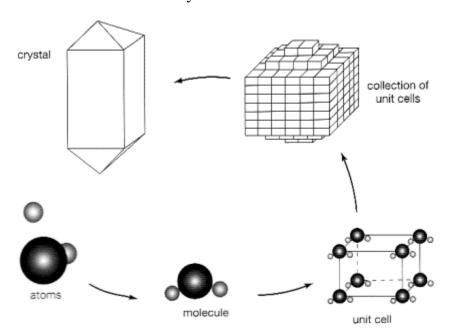




Atoms and Elements

Read Chapter 4 of Klein & Philpotts or Read Chapter 3 of Nesse (2000)

atoms \rightarrow molecules \rightarrow crystals \rightarrow rocks \rightarrow Earth



http://darkwing.uoregon.edu/~cashman/GEO311/311pages/L1-Intro pic files/image014.gif

Element: A chemical element is a pure chemical substance consisting of one type of atom distinguished by its atomic number, which is the number of protons in its nucleus. (http://en.wikipedia.org/wiki/Chemical_element)

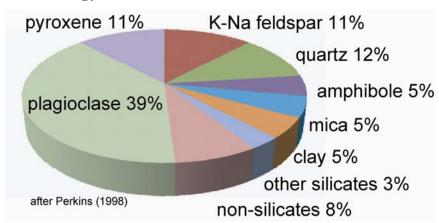
Common mineral-forming elements

Elemental composition of the whole Earth and the crust (the outermost solid layer):

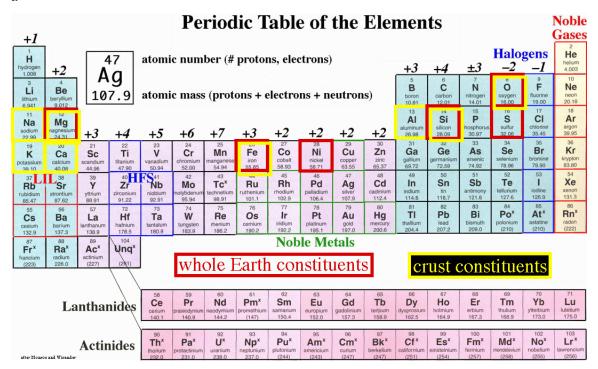
element	whole Earth	crust	mineral
О	29%	46%	most minerals
Si	15%	28%	silicates
Al	1%	8%	feldspar
Fe	35%	6%	pyroxene, amphibole

Ca	1%	4%	plagioclase
Na	<1%	2%	feldspar
Mg	11%	2%	olivine
K	<1%	2%	K-feldspar
S	<3%	<1%	pyrite
Ni	2%	<1%	olivine

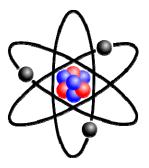
mineralogy of Earth's crust



a



Atoms



atom: The smallest particle that retains the chemical properties of an element; composed of

proton: electric charge +1, 1.00728 amu **neutron**: electric charge 0, 1.00867 amu

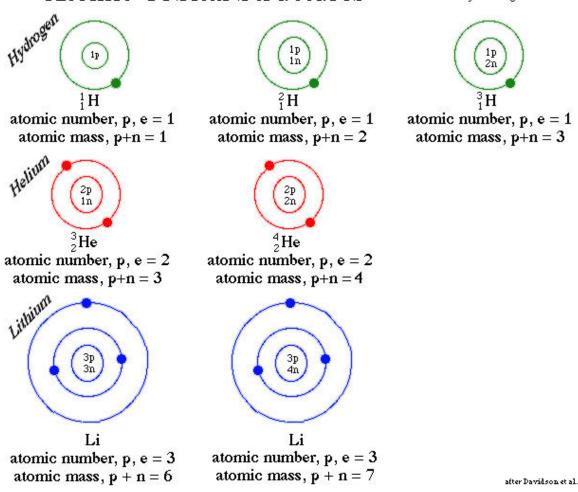
electron, e-: electric charge -1, 0.00055 amu (insignificant)

For example, Li has an **atomic number** of 3, meaning 3 protons (and 3 electrons, if neutral); if it is 7Li, it has a mass of 7 and thus 4 neutrons. electrons fill orbital levels around the **nucleus**: 2 in the first level, 8 in the second, and so on

the position of an element in the periodic table relates to the number of electrons in the **outer orbital**

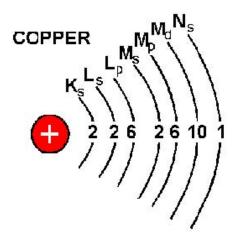
Atomic Orbital Structures

*naturally occuring



Structure of Atoms

The four electron shells surrounding the nucleus are named—with increasing distance and energy—K (or 1), L (or 2), M (or 3), and N (or 4) shells. Each shell is split into subshells, labeled s, p, d, and f; the K shell contains an s subshell, the L shell has s and p subshells, M has s, p, and d, and N has s, p, d, and f. An s subshell consists of one s orbital (with 2 electrons), a p subshell consists of up to 3 p orbitals (6 electrons), and a d subshell consists of up to 5 d orbitals (10 electrons).

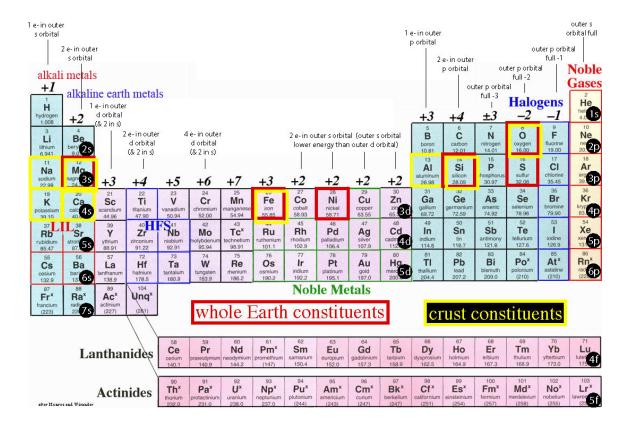


this is written 1s² 2s² 2p6 3s² 3p6 4s¹ 3d¹0

electronic configurations

					sh	ıell			
(±)		K	L	L	\mathbf{M}	\mathbf{M}	\mathbf{M}	\mathbf{N}	N
Z el	ement	1S	2 S	2 p	3s	3p	3d	4 S	4p
1	Η	1							
2	He	2							
_									
3	Li	2	1						
4	Be	2	2						
5	В	2	2	1					
6	C	2	2	2					
7 8	N	2	2	3					
	O	2	2	4					
9	F	2	2	5					
10	Ne	2	2	6					
11	Na	2	2	6	1				
12	Mg	2	2	6	2				
13	Al	2	2	6	2	1			
14	Si	2	2	6	2	2			
15	P	2	2	6	2	3			
16	S	2	2	6	2	4			
17	Cl	2	2	6	2	5			
18	Ar	2	2	6	2	6			
19	K	2	2	6	2	6		1	
20	Ca	2	2	6	2	6		2	
21	Sc	2	2	6	2	6	1	2	
22	Ti	2	2	6	2	6	2	2	
23	V	2	2	6	2	6	3	2	

36	Kr	2	2	6	2	6	10	2	6
35	Br	2	2	6	2	6	10	2	5
34	Se	2	2	6	2	6	10	2	4
33	As	2	2	6	2	6	10	2	3
32	Ge	2	2	6	2	6	10	2	2
31	Ga	2	2	6	2	6	10	2	1
30	Zn	2	2	6	2	6	10	2	
29	Cu	2	2	6	2	6	9	2	
28	Ni	2	2	6	2	6	8	2	
27	Co	2	2	6	2	6	7	2	
26	Fe	2	2	6	2	6	6	2	
25	Mn	2	2	6	2	6	5	2	
24	Cr	2	2	6	2	6	4	2	



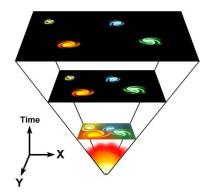
Ions

elements tend to gain or lose electrons to acquire the configuration of a noble gas

cation: ion w/ excess + charge
anion: ion w/ excess - charge

typical oxidation states: http://www.wsu.edu/~wherland/#Radii

Cosmochemistry and the production of elements



(for more see http://en.wikipedia.org/wiki/Stellar nucleosynthesis)

The birth of matter in the universe began about 15–20 Ga, judged by tracing expanding galaxies (groups of stars) back to a common origin in the Big Bang After 1 m.y., the universe had cooled sufficiently (3000K) for H and He to form from subatomic particles

These elements aggregated to form stars via gravitational attraction; stars are 75 wt% H, 22 wt% He, and 3% heavier elements

The heat of star aggregation caused particles and elements to accelerate and collide, forming elements as heavy as Fe (atomic number 26)

Elements heavier than Fe are produced by during supernovae explosions, which occur when the gravitational force of the outer layers of a star overcomes the thermal pressure of the fusing inner layers



Carbon burning

 $^{12}\text{C} + ^{12}\text{C} -> ^{20}\text{Ne} \text{ or } ^{23}\text{Na or } ^{23}\text{Mg or } ^{24}\text{Mg or } ^{16}\text{O}$

carbon is consumed and a core of product elements builds up; gravity builds up and the new core collapses sufficiently to burn heavier elements

Oxygen burning

¹⁶O + ¹⁶O -> ²⁸Si or ³¹P or ³¹S or ³⁰Si or ³⁰P or ³²S or ²⁴Mg O, Ne, Mg, Si, S burning takes a star 6 months, reaching 3E9 Kelvin

The heat of star aggregation causes particles and elements to accelerate and collide, forming elements as heavy as Fe (atomic number 26).

Silicon burning

lasts one day, reaching 5E9 Kelvin. This causes a gravitational collapse, forming either a neutron star or a black hole, with the outer layers being blown off in a supernova whose neutron burst forms elements heavier than Fe

$$^{28}\text{Si} + ^{4}\text{He} -> ^{32}\text{S}$$

$$32S + 4He -> 36Ar$$

$$^{36}Ar + ^{4}He -> ^{40}Ca$$

$$^{48}\text{Cr} + ^{4}\text{He} -> ^{52}\text{Fe}$$

$$52 \text{Fe} + 4 \text{He} -> 56 \text{Ni}$$

Further accretion formed solar systems, meteorites, and planets by about 4.5 Ga Differentiation of the Earth occurred by gravitational separation of the lightest elements into the atmosphere and the densest elements into the core.

Chemical Bonds

What is a molecule?

Molecule: group of bonded atoms; e.g., H₂O, SiO₂, NaCl

What is a mineral?

Mineral: a solid of specific composition with a regular arrangement of atoms

How do atoms **bond** together to form minerals? Elements bond by sharing or transferring electrons

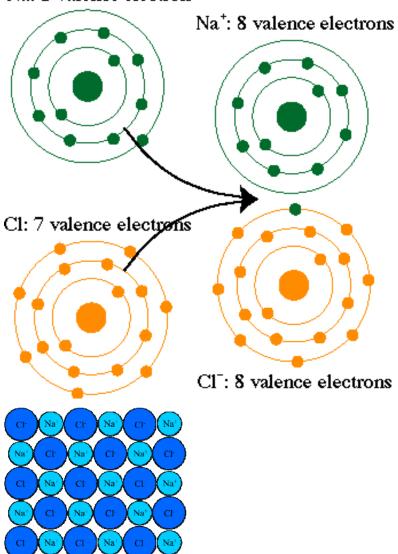
Why don't elements prefer to remain alone, unbonded? Elements like to have their outer electron orbital full of electrons, so elements with full orbitals are very stable (e.g., the noble gases He, Ar, Kr, Xe) elements near the left side of the periodic table (e.g., this creates the positively charged ions K+, Mg²⁺) like to give up electrons (the next lower orbital becomes full), while those near the right side like to gain electrons to become full (e.g., this creates the negatively charged ions S²⁻, Cl⁻)

ionic bond: electrostatic attraction between cations and anions; forms where and when, e.g.,

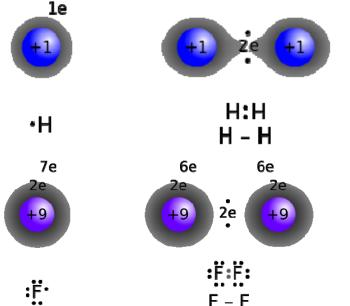
- one atom that loses an electron to become a more-stable cation is adjacent to second atom that gains an electron to become a more-stable anion (e.g., NaCl);
- one atom that loses two electrons to become a more-stable cation is adjacent to second and third atoms that gain an electron to become a more-stable anion (e.g., CaCl₂);

the atoms are attracted and bound to one another by electrostatic charge nice movie of this at http://en.wikipedia.org/wiki/Ionic_bond an ionic bond is charge balanced soluble in H2O because, e.g., NaOH and HCl are more stable than NaCl + H2O; ionic solids are hygroscopic, and can dissolve in H2O pulled out of the atmosphere; also have low melting point

Na: 1 valence electron

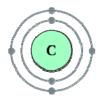


covalent bond: sharing of electrons between atoms when orbitals overlap; 'beneficial' for atoms that can fill their valence shell



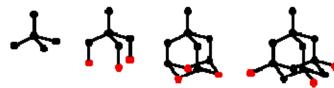
http://en.wikipedia.org/wiki/Covalent_bond

e.g., carbon would "like to have" 6 electrons in its valence shell, but has only 2



from http://en.wikipedia.org/wiki/Covalent_bond

if it can share valence electrons with 3 other C atoms in a 4-fold, 4-coordinated, tetrahedral structure, it can be electrically neutral. This is diamond

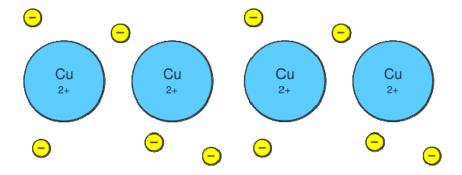


http://www.chemguide.co.uk/atoms/structures/giantcov.html

Si is right below C in the periodic table, so also "missing" 4 electrons in its valence shell

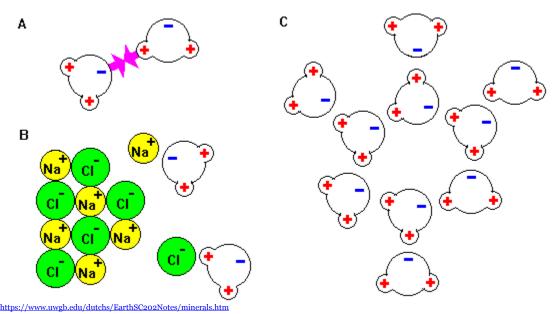
so, metallic Si has the same structure as diamond another configuration for Si is that of quartz, SiO_2 , in which each Si^{4+} cation is charge balanced by four half oxygen atoms, O^{2-} covalently bonded materials are insoluble in H_2O and have high melting temperatures

metallic bond: special type of covalent bond in which valence electrons are freer to migrate around multiple atoms in "multi-atom orbitals"



leads to materials that are electrically conductive, strong yet malleable, and have high melting temperatures (except for the Zn–Cd–Hg group, which are close to noble gases in their electronic configuration)

hydrogen bond: weak electrostatic attraction among individual polar molecules (e.g., H₂O)

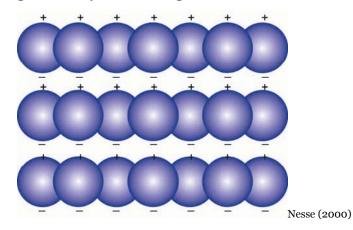


unusually high heat capacity, making H2O the principal heat reservoir in Earth expands when freezing; very weird complexes with many ions; great solvent of ionic bonds

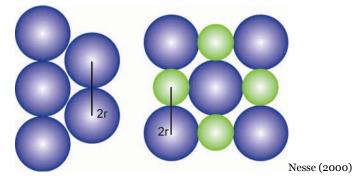
van der Waals bond: weak electrostatic attraction between dipoles—or all forces not covered by the aforementioned types of bonding



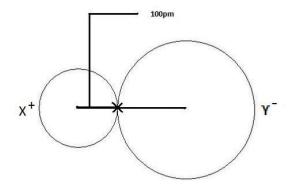
geckos may climb using van der Waals forces



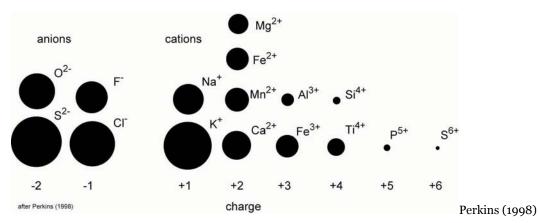
bond length: distance between atoms that are bonded



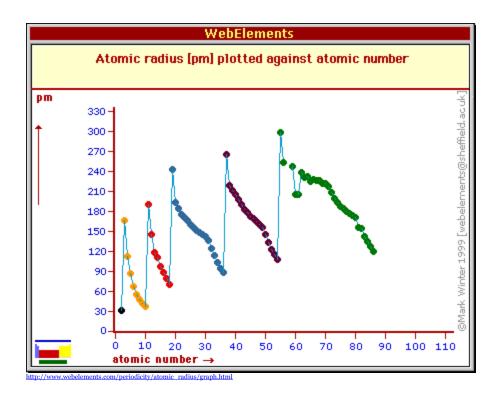
effective radius of an atom is its size within a crystal lattice



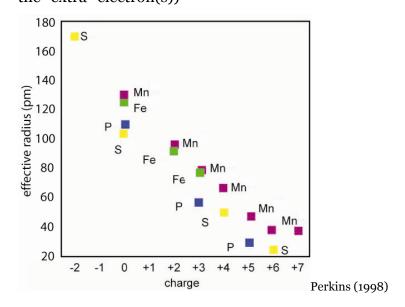
http://chemwiki.ucdavis.edu/Inorganic Chemistry/Descriptive Chemistry/Periodic Table of the Elements/Atomic Radii



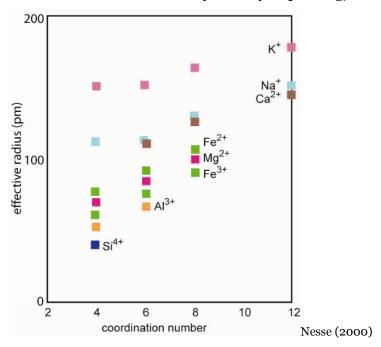
decreases from left to right across periodic table as the number of electrons and protons increase and exert an increasing mutually attractive force increases down the periodic table (from a noble gas to an alkali metal) due to the addition of another electron shell)



effective radius is affected by oxidation state, with cations smaller than the neutral atom (because of the "missing" electron(s)) and anions larger (because of the "extra" electron(s))



effective radius is affected by density of packing/coordination



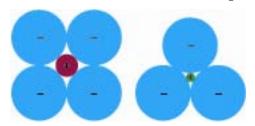
this is encapsulated in the Goldschmidt correction:

coordination number	radius
XII	1
VIII	0.97
VI	0.96
IV	0.88

high-coordination materials are denser; even though the anions are a *bit* farther from the cation, the number of anions nearer the cation is larger

Pauling's Rule 1 (Radius Ratio Principle)

cation—anion separation = cation radius + anion radius cation coordination number depends on cation radius / anion radius



coordination number	cation radius / anion radius		
XII	1		
VIII	0.73-1		
VI	0.41-0.73		
IV	0.22-0.41		
III	0.15-0.22		

Pauling's Rule 2 (Electrostatic Valency Principle) bond strength = ionic charge /coordination number

Crystal Structure

Read Chapters 4 & 5 of Klein & Philpotts or Read Chapter 4 of Nesse (2000)

If Si and O are the most common elements in the outer part of the Earth, what are common minerals made of?

silicates are the most common minerals because O is the most common anion and Si is the most common cation; hence SiO₄ and variants

How do Si and O bond together to form 3-D structures? Is SiO_4 a stable compound?

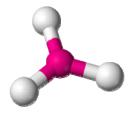
SiO₄ has a net negative charge of 4-; this must be balanced by cations

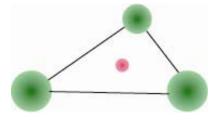
the minimum **coordination number** for an element that is part of a 3D mineral is IV, thus SiO4, (cannot form 3-D structures from 3-coordinated things like CO₃)

What structure can be formed from pure Si and O?

Quartz: SiO₂ in a 3-D array of tetrahedra, each of which is joined to other tetrahedra at all 4 corners; quartz is 100% SiO₂ and has a density of 2.65 g/cm³

coordination number: number of atoms surrounding another
3-fold, III, planar

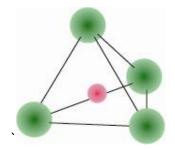




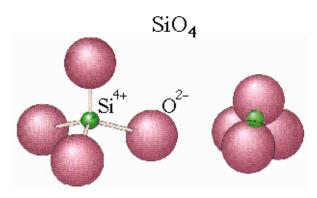
example material: $\mathrm{BO_3^{3-}}$, $\mathrm{SO_3}$, $\mathrm{NO_3^-}$, $\mathrm{CO_3^{2-}}$

4-fold, IV, tetrahedral; common





tetrahedron, with 3 triangular faces

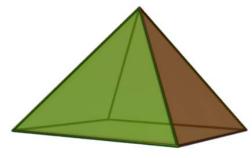


expanded for clarity

true scale

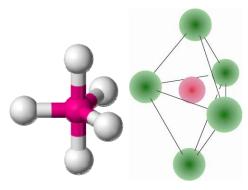
example mineral: Si in many silicates is surrounded by 4 O

5-fold, V; uncommon

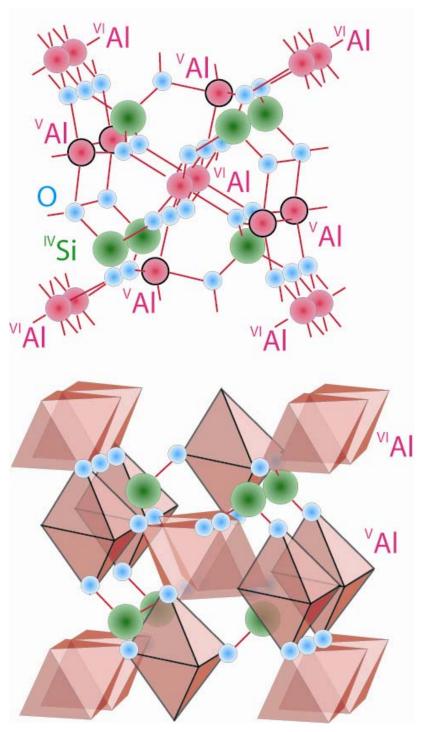




square pyramid, with 4 triangular faces and 1 square face

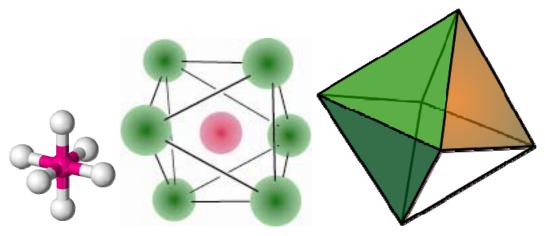


trigonal bipyramid, with 6 triangular faces

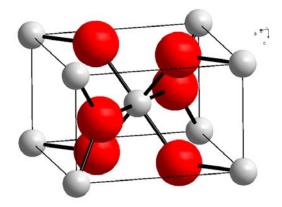


example mineral: half the Al in and alusite is surrounded by 5 $\rm O$

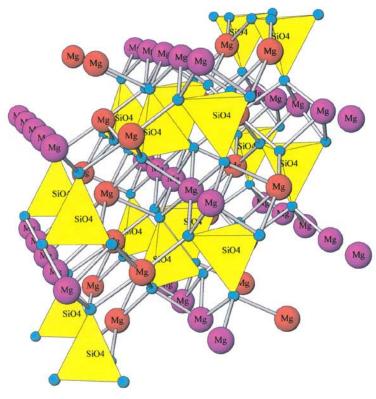
6-fold, VI, octahedral; common



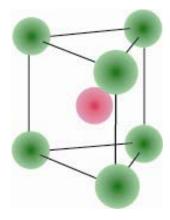
octahedron, with 8 triangular faces



example mineral: Ti in rutile is surrounded by 6 O atoms



http://www3.geosc.psu.edu/courses/Geosc533/LectureMaterials/Lecture11/Olivine_structure_1.html example mineral: Mg or Fe in olivine is surrounded by 6 O atoms

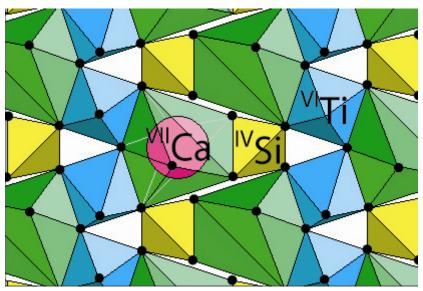


triangular prism, with 2 triangular faces and 3 square faces example mineral: Mo in molybdenite is surrounded by 6 S atoms

7-fold, VII; uncommon



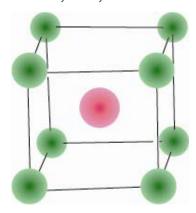
pentagonal bipyramid, with 10 triangular faces



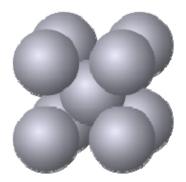
 $\underline{http://www.uwgb.edu/dutchs/Petrology/Titanite\%20Structure.HTM}$

example mineral: Ca in titanite is surrounded by 7 O atoms

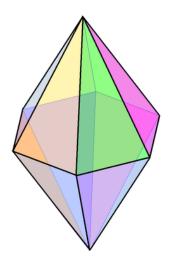
8-fold, VIII; common



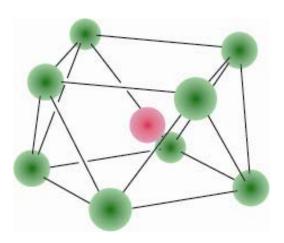
prism, with 6 rectangular faces:



body-centered cubic packing: cube with 6 square faces example mineral: metallic Fe, Cr, Mo, W, V, Nb, Ta; strong, less ductile atomic packing factor (volume of atoms/volume of unit cell) = 0.68



hexagonal bipyramid with 12 triangular faces





square antiprism with 8 triangular faces and 2 square faces

example mineral: Ca in scheelite is surrounded by 8 oxygen

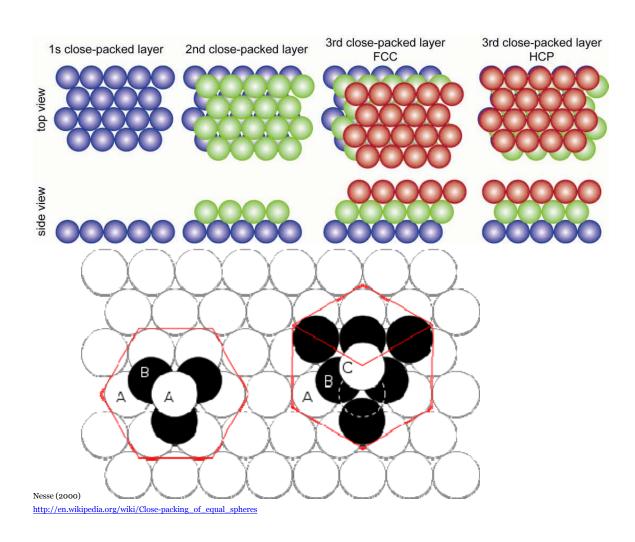
12-fold, XII; common

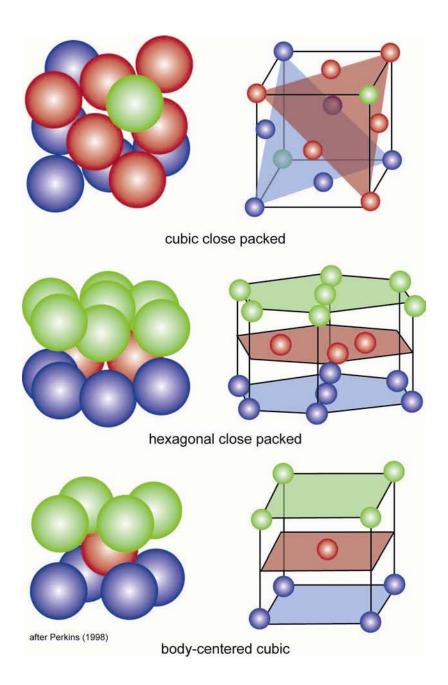
close packing

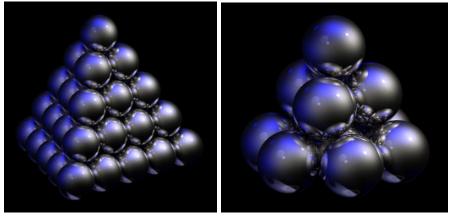
because metals share electrons freely, they can attain close packing Here's a helpful animation to see how cannonballs stack to make tetrahedra in case you have never served on a pirate ship:

http://upload.wikimedia.org/wikipedia/commons/3/32/Animated-HCP-Lattice.gif

hexagonal closest packing 12 neighboring atoms face-centered cubic packing 12 neighboring atoms atomic packing factor (volume of atoms/volume of unit cell) = 0.74







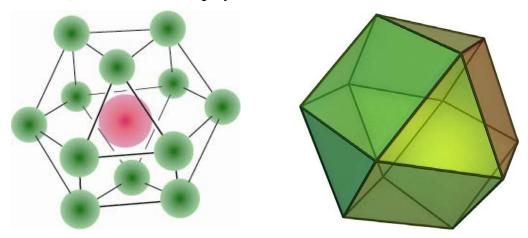
FCC HCP

the key to seeing the difference is that the two balls in the 2^{nd} layer from the top touch different balls in the 3^{rd} layer from the top and that the adjacent balls along each edge of the tetrahedron defined by the stack are (FCC) or are not (HCP) in direct contact with each other

example **FCC** mineral: metallic Cu, Ag, Au, Pb, Co, In, Rh, Pd, Ir, Pt; soft and ductile

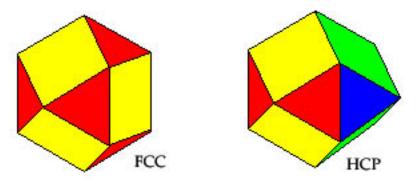
example HCP mineral: metallic Sc, Ti, Y, Zr; usually brittle

for **FCC**, the coordination polyhedron is



cuboctahedron, with 8 triangular faces and 6 square faces

for **HCP** the coordination polyhedron is similar to FCC, but with half rotated 60°

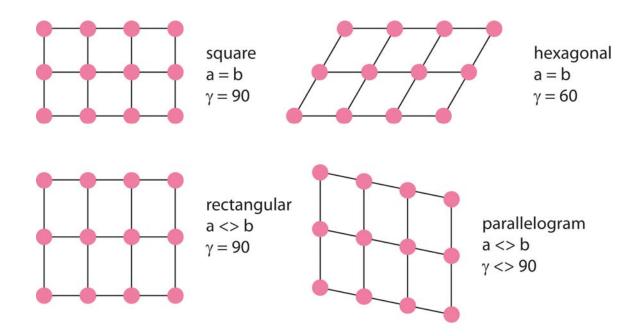


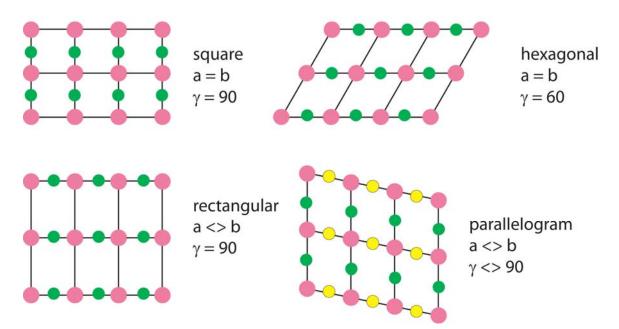
http://www.uwgb.edu/dutchs/Petrology/coordination.htm

Lattices, Symmetry, Point Groups, Space Groups

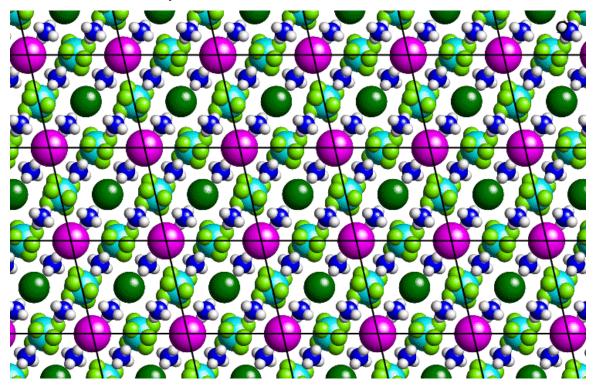
Read Chapter 5 of Klein & Philpotts or Read Chapter 2 of Nesse (2000)

plane lattice: a 2D pattern of atoms (or points or objects) that extends infinitely

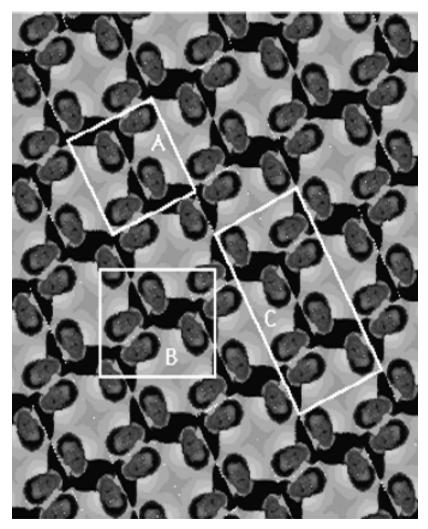




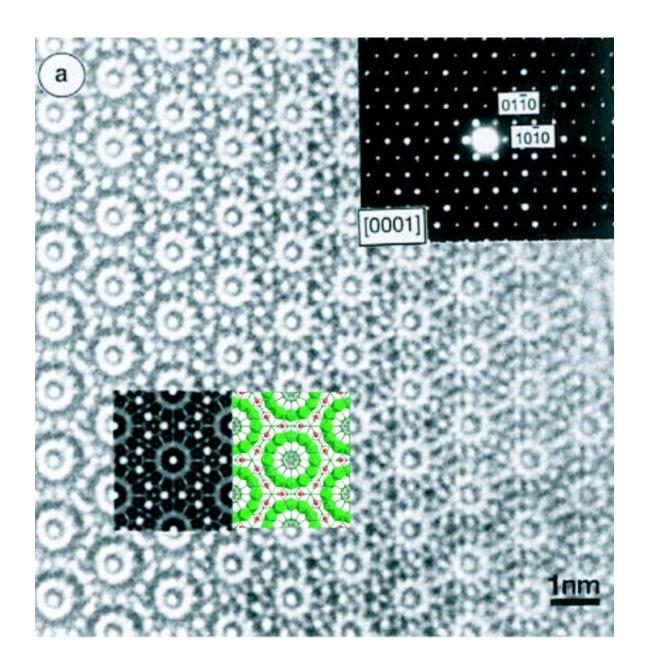
2D 'unit cell': minimum portion of lattice required to describe 'crystal' (may be more than once choice)



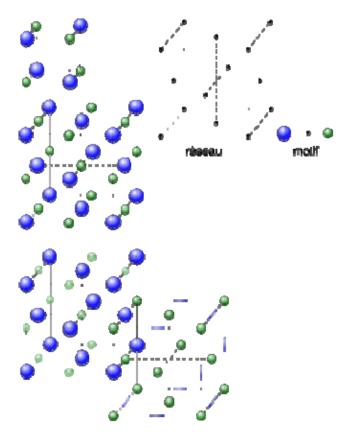
http://pd.chem.ucl.ac.uk/pdnn/symm1/trans1.htm



 $\underline{\text{http://depts.washington.edu/chemcrs/bulkdisk/chem484A spro6/notes Slides 1 Lattice-2-D CHEM484Aspro6.pdf}}$

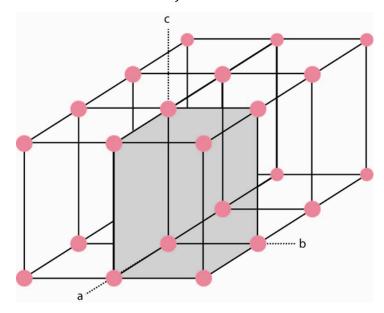


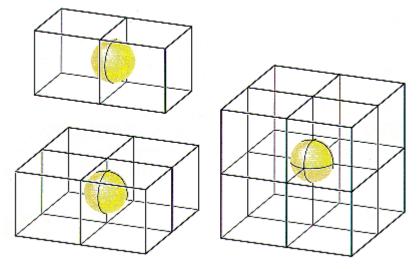
space lattice: a 3D pattern of atoms that extends infinitely



crystal axes: vectors defined by the unit cell

unit cell: minimum portion of space lattice required to describe crystal (may be more than once choice)



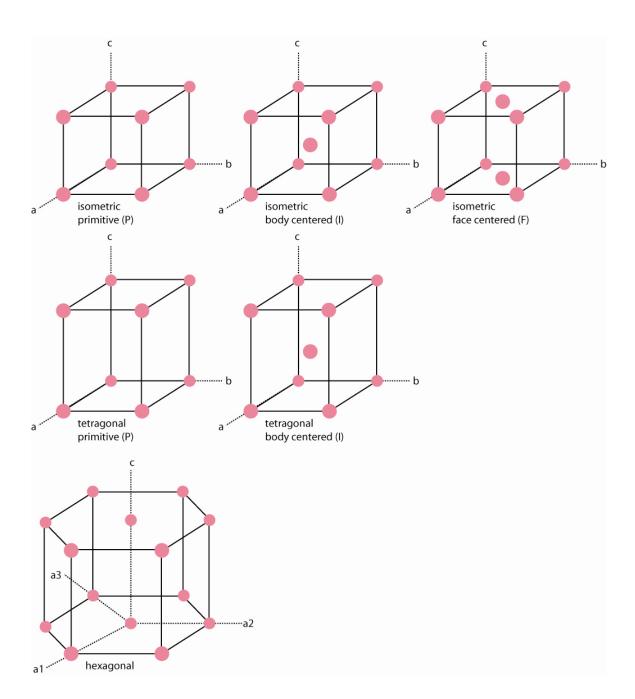


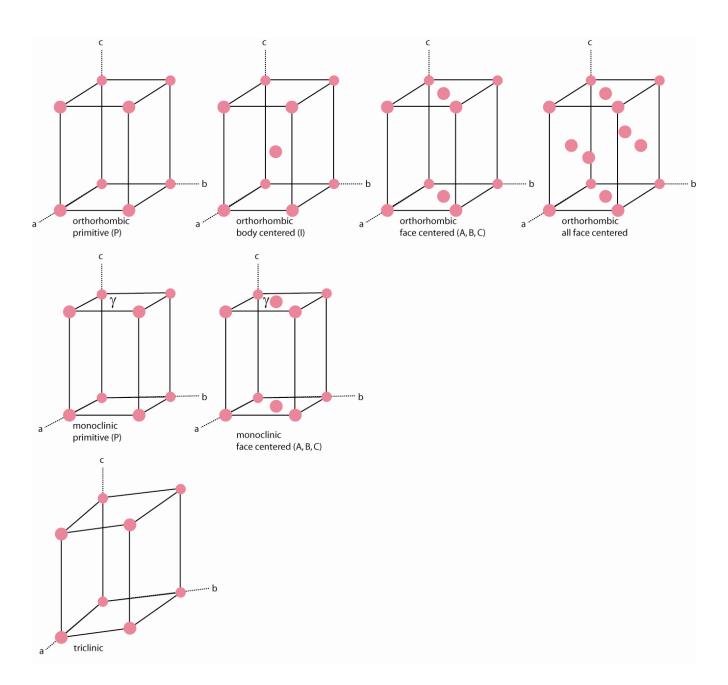
 $\frac{\text{http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch13/unitcell.php}}{\text{atoms at corners of cells are shared among cells}}$

There are six types of unit cell:

isometric	a = b= c	$\alpha = \beta = \gamma = 90^{\circ}$
hexagonal	a ≠ c	$\alpha = 90^{\circ} \gamma = 60^{\circ}$
tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$
orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$
monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^{\circ} \neq \beta$
triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma$

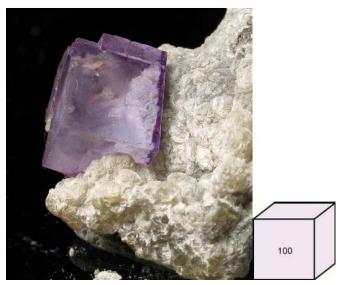
The distribution of atoms in the unit cell (P, primitive; F, face centered; I, body centered or Innenzentrierte) gives rise to the 14 **Bravais lattices** see http://commons.wikimedia.org/wiki/Crystal_structure







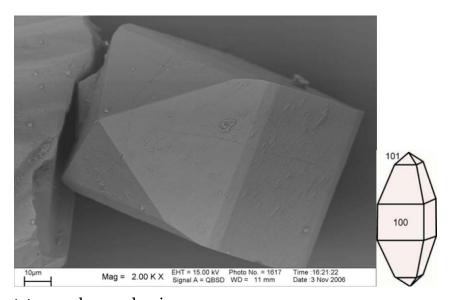
cubic example: garnet



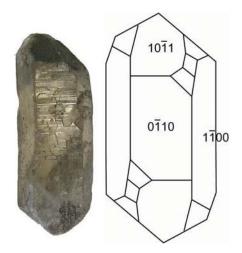
cubic example: fluorite



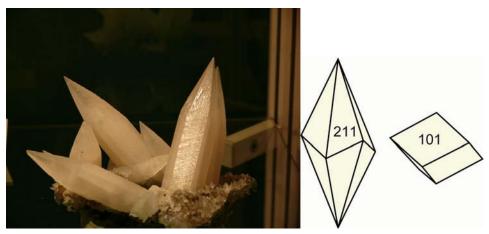
tetragonal example: rutile



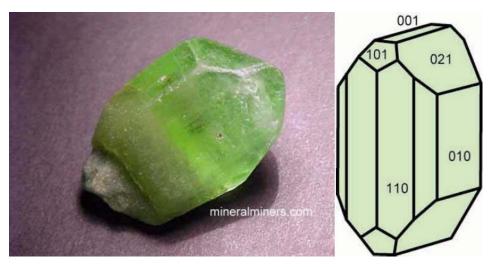
tetragonal example: zircon



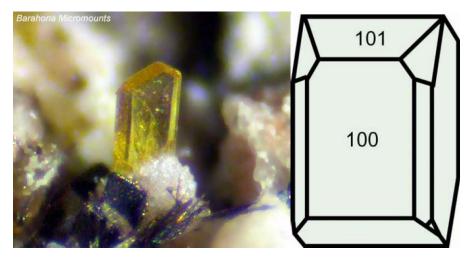
hexagonal example: quartz



hexagonal example: calcite



 $or tho rhombic\ example:\ olivine\ {\it (from\ www.mineral miners.com/.../mins/perm111.jpg)}$



monoclinic example: diopside



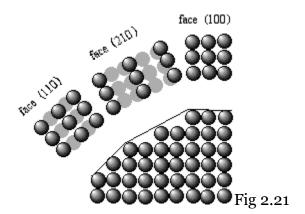
triclinic example: albite

see

http://www.uwsp.edu/geo/projects/geoweb/participants/dutch/symmetry/unitc ell.htm for some nice examples of how crystal forms are made up of unit cells

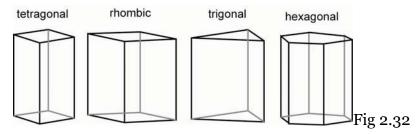
Crystal Faces

crystal faces tend to be close-packed planes of atoms



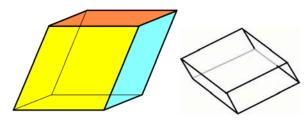
prism

set of faces parallel to one direction



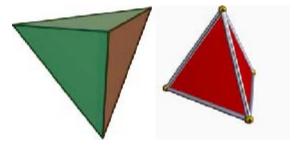
rhombohedron

6 rhomb-shaped faces like a stretched or squashed cube part of F2.33

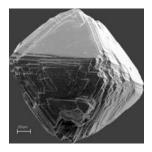


tetrahedron

4 triangular faces



octahedron



for more crystal forms see

http://www.uwsp.edu/geo/projects/geoweb/participants/dutch/symmetry/xlforms.htm

Point symmetry and Point Groups

Point symmetry operations in 2D are

reflection

like a mirror

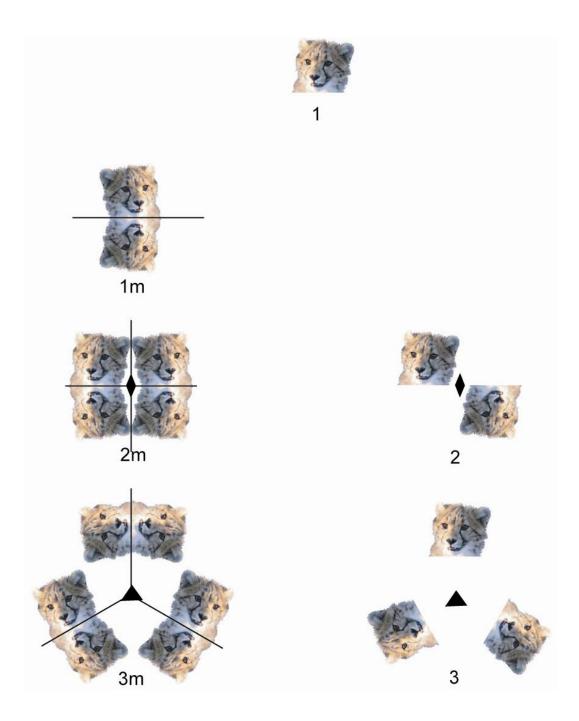


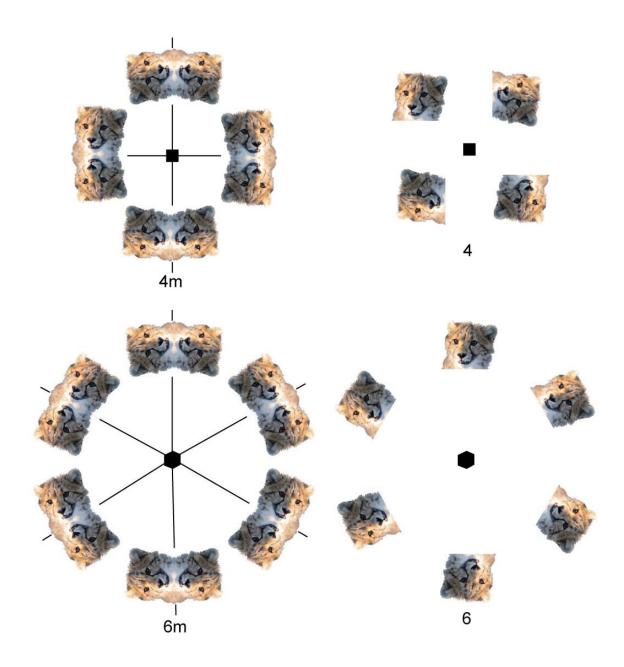


rotation

around an axis; number identifies degrees of rotation as 360°/n

reflection and rotation produce the 10 2D **point groups**, each of which consists of a rotation axis or a rotation axis plus a mirror parallel to that axis (i.e., the mirror normal is perpendicular to the rotation axis)

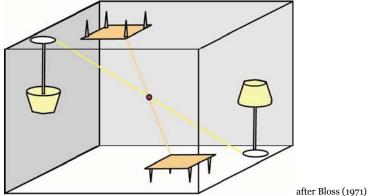




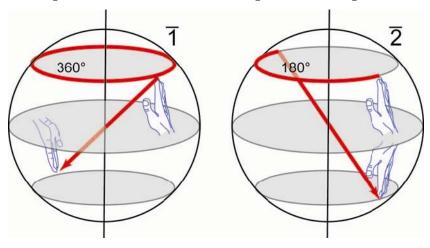
Adding a $3^{\rm rd}$ dimension permits a $3^{\rm rd}$ symmetry operation:

rotoinversion (rotation + inversion)

rotoinversion axes have a bar over the top of the number to distinguish them from ordinary rotation axes; axis of rotation is perpendicular to mirror plane



- $\overline{1}$ rotoinversion is a simple **center of symmetry** like the room drawing above.
- $\overline{2}$ is equivalent to a mirror plane.
- 6 is equivalent to a 3-fold rotation plus a mirror plane



this leads to the 32 **space groups** or **crystal classes**, with their **Hermann–Mauguin** symbols

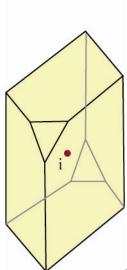
HM symbols show non-redundant symmetry operations

There are 3 "digit" positions, each of which indicates the orientation of a symmetry element (if a mirror and rotation have the same orientation, they are denoted "n/m", meaning that the mirror is perpendicular to the rotation axis—or the mirror normal is parallel to the rotation axis):

crystal system	1st symbol	2nd symbol	3rd symbol
cubic	$4, 4/m, \overline{4}, 2, 2/m$	$3, \overline{3}$	2, 2/m, m

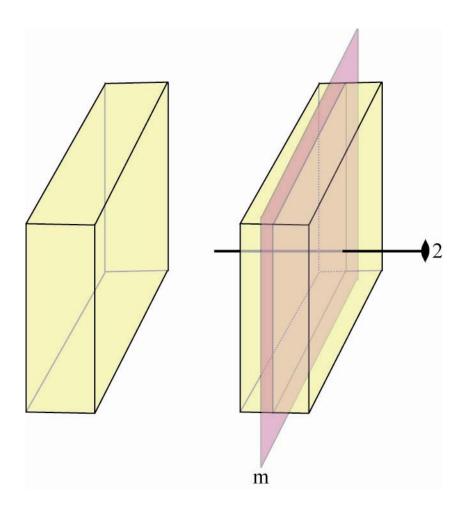
hexagonal	$6, 6/m, \overline{6}, 3, 3$	2/m, m	2, 2/m, m
tetragonal	4, 4/m, 4	2, 2/m, m	2, 2/m, m
orthorhombic	2, 2/m, m	2, 2/m, m	2, 2/m, m
monoclinic	2, 2m, m		
triclinic	1, 1		

Triclinic (e.g., $\overline{1}$)

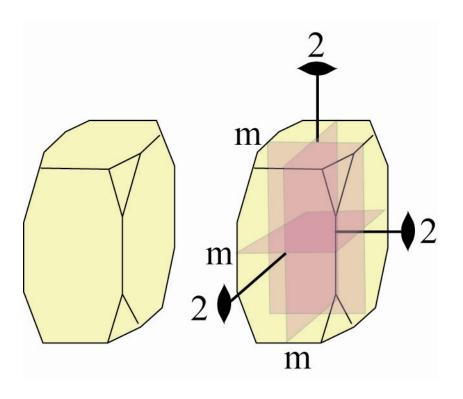


 $after\ \underline{http://www.tulane.edu/\sim}sanelson/\underline{eens211/32crystalclass.htm}$

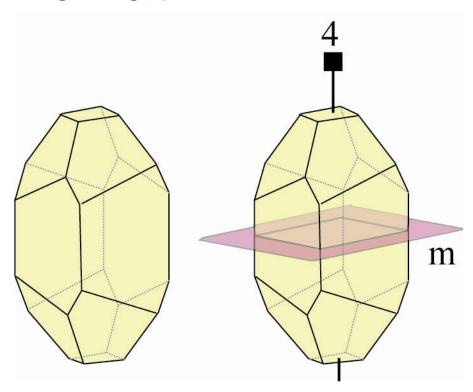
Monoclinic (e.g., 2/m)



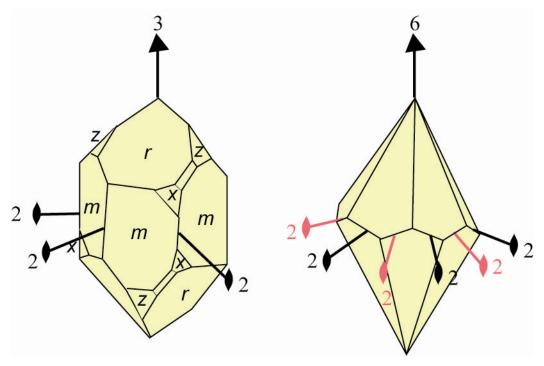
Orthorhombic (e.g., 2/m 2/m)



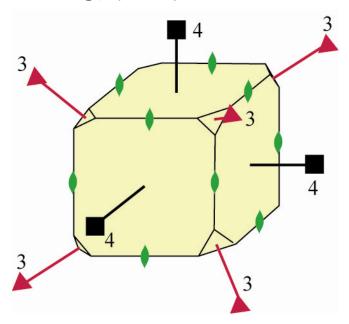
Tetragonal (e.g., 4/m)



Trigonal (e.g., 3 2; α quartz) and hexagonal (e.g., 6 2 2; β quartz)



Cubic (e.g., $4/m \overline{3} 2/m$)

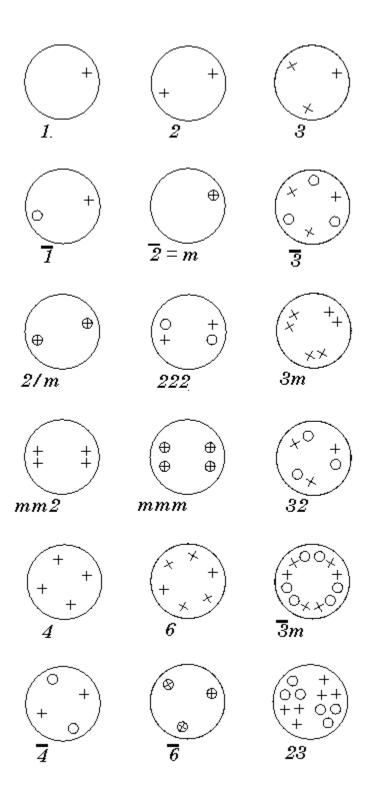


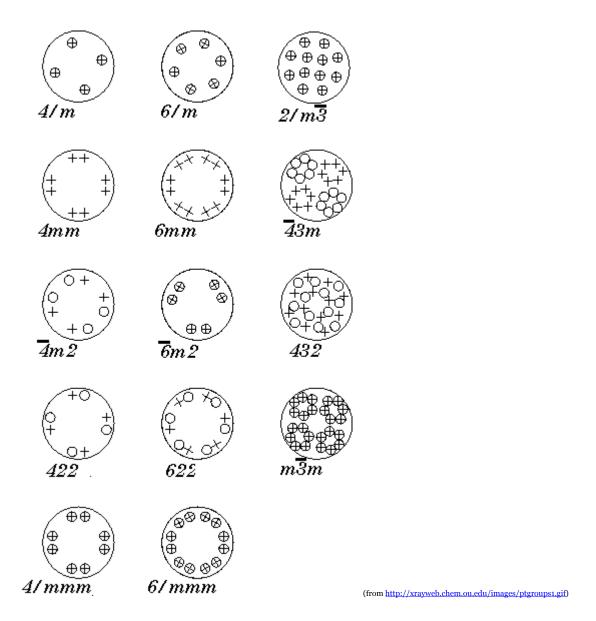
Crystal System	Crystal Class, H–M	Name of Class
Triclinic		pedial
		pinacoidal
Monoclinic	2	sphenoidal

	m	domatic	
	2/m	prismatic	
	222	rhombic-disphenoidal	
Orthorhombic	mm2 (2mm)	rhombic-pyramidal	
	2/m2/m2/m	rhombic-dipyramidal	
	4	tetragonal- pyramidal	
	4	tetragonal-disphenoidal	
	4/m	tetragonal-dipyramidal	
Tetragonal	422	tetragonal-trapezohedral	
	4mm	ditetragonal-pyramidal	
	42m	tetragonal-scalenohedral	
	4/m2/m2/m	ditetragonal-dipyramidal	
	3	trigonal-pyramidal	
	3	rhombohedral	
	32	trigonal-trapezohedral	
	3m	ditrigonal-pyramidal	
	32/m	hexagonal-scalenohedral	
Hexagonal	6	hexagonal-pyramidal	
Hexagonar	ē	trigonal-dipyramidal	
	6/m	hexagonal-dipyramidal	
	622	hexagonal-trapezohedral	
	6mm	dihexagonal-pyramidal	
	<u>6</u> m2	ditrigonal-dipyramidal	
	6/m2/m2/m	dihexagonal-dipyramidal	
	23	tetaroidal	
	$2/m\overline{3}$	diploidal	
Isometric	432	gyroidal	
	43m	hextetrahedral	
	4/m 32/m	hexoctahedral	

http://www.tulane.edu/~sanelson/eens211/32crystalclass.htm

the 32 **space groups** or **crystal classes** can be represented by stereonets

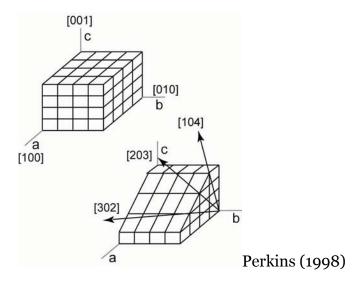




Miller indices are used to describe crystal faces and directions

Directions

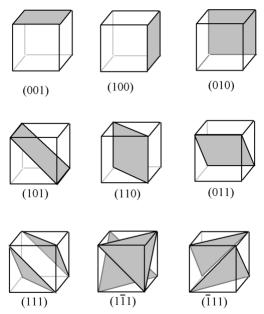
Miller indices for directions are integers that describe the vector representation of the direction; e.g., [104] is the direction that points 1 unit cell in the a direction and 4 unit cells in the c direction and is parallel to the b axis. [uvw] describes a specific direction; <uvv> is a family of crystallographically equivalent directions



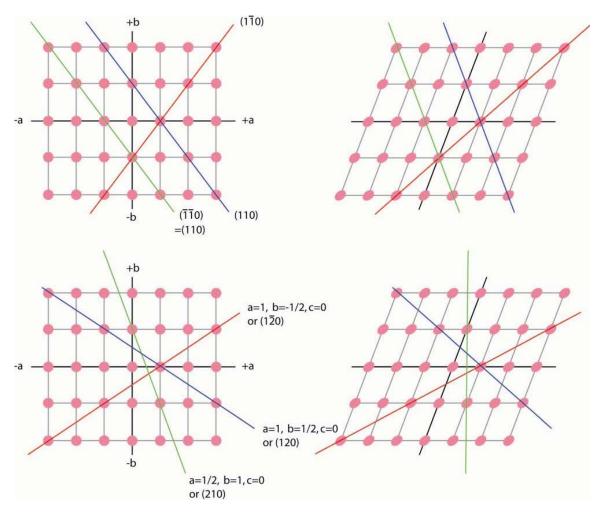
Planes

Miller indices for planes are integers that are the *reciprocal* of the intersection with each axis; e.g., (104) is the plane that intersects the a axis at 1 unit-cell spacing and the c axis at 1/4 unit-cell spacing and is parallel to the b axis.

Like H–M symbols, a bar is used to indicate a negative number.



(hkl) describes a specific plane; {hkl} is a family of crystallographically equivalent planes



somewhat more painful in the hexagonal system

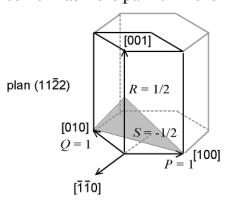


Fig 2.24 [uvtw] describes a specific direction; <uvtw> is a family of crystallographically equivalent directions t = -(u+v)

(hkil) describes a specific plane; $\{hkil\}$ is a family of crystallographically equivalent planes i = -(h+k)

Crystal Structures

Read Chapter 20, Chapters 11–19 of Nesse (2000)

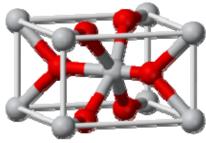
Hydroxides

'bauxite' (several minerals)	Al hydroxide	source of Al
goethite	Fe hydroxide	rust



X4+O₂ group

rutile	VITiO ₂	tetragonal	source of Ti
cassiterite	VISnO ₂	tetragonal	source of Sn
uraninite	$VIIIUO_2$	cubic	source of U



http://en.wikipedia.org/wiki/Rutile
rutile (cassiterite) has a body-centered tetragonal structure with VITi (VISn)

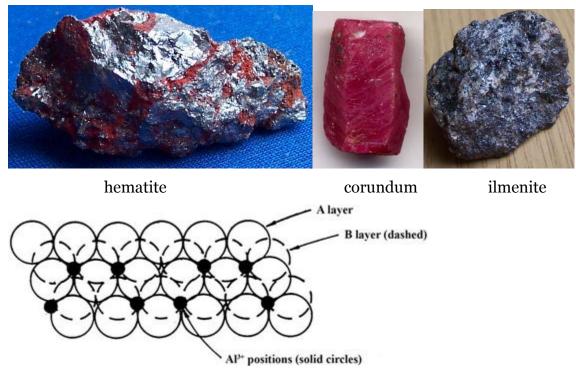


VIX3+2 O3 group

trigonal

oxygen in approximately hexagonal closest packing, with cations in 2/3 of the 'holes'

hematite	Fe ³⁺ ₂ O ₃	rust; source of Fe	
corundum	$Al^{3+}{}_2O_3$	source of Cr (ruby)	
ilmenite	Fe ²⁺ Ti ⁴⁺ O ₃	source of Fe	



http://www.chegg.com/homework-help/questions-and-answers/corundum-crystal-structure-al2o3-consists-hcp-arrangement-o2-ions-al2-ions-occupy-octahedr-q1339240-ions-occupy-octahedr-q1339240-ions-al2-ions-occupy-octahedr-q1339240-ions-occupy

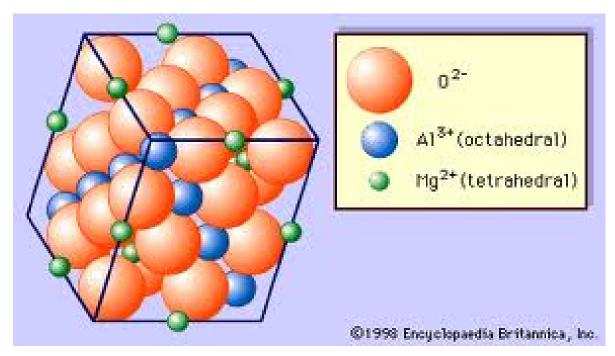
Spinel Group ${}^{\text{IV}}X^{2+\text{VI}}Y^{3+}{}_{2}O_{4}$

cubic

00.010		
spinel	MgAl ₂ O ₄	
chromite	FeCr ₂ O ₄	source of Cr
magnetite	Fe ²⁺ Fe ³⁺ ₂ O ₄	source of Fe



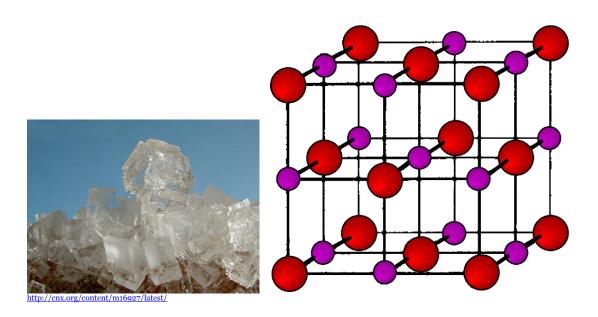
spinel chromite magnetite



spinel structure consists of cubic close packed oxygen

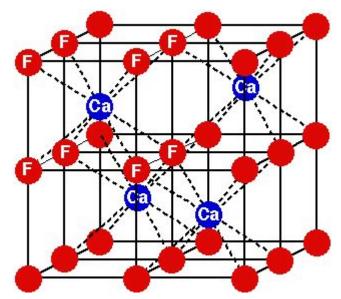
Halide Minerals

halite	^{VI} NaCl	cubic
sylvite	KCl	cubic; source of K
fluorite	VIIICaF ₂	cubic; source of F



halite (Na^+ (green) coordinated with six Cl^- (orange); Na and Cl alternate in a face-centered cubic arrangement





 $http://www.seas.upenn.edu/{\sim}chem101/sschem/ionicsolids.html\#fluorite$

fluorite structure; face-centered cubic structure with half of the cubic sites filled. Ca^{2+} (grey) coordinated with eight F^- (yellow)

Sulfide Minerals

sphalerite	^{IV} ZnS	cubic; source of Zn
galena	VIPbS	cubic; source of Pb
pyrite	^{VI} FeS	cubic
cinnabar	VIHgS	source of Hg
molybdenite	VIMoS ₂	hexagonal; source of Mo







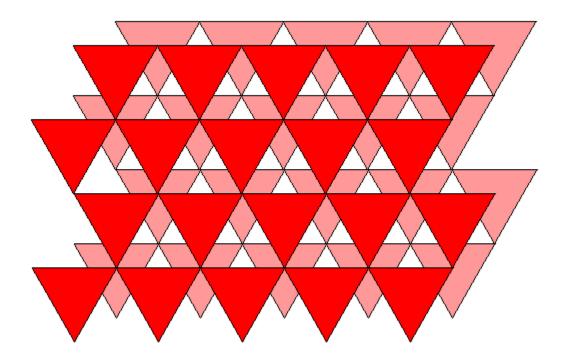
sphalerite

galena

pyrite

pyrite structure similar to that of NaCl

molybdenite structure consists of pairs of triangular S sheets with Mo in between in triangular prisms with 6-fold coordination; weak van der Waals bonds hold the sheets together



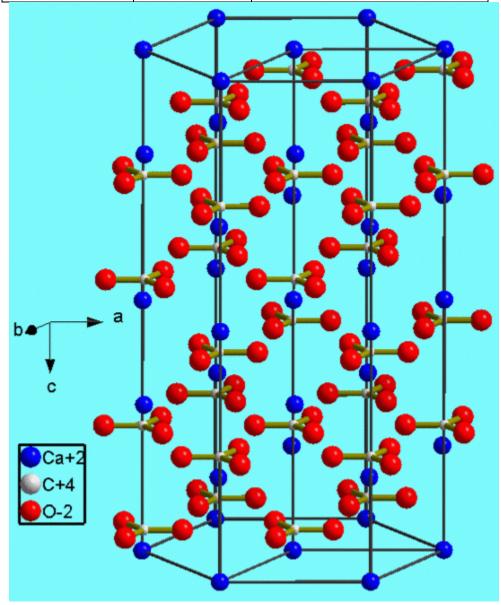
 $\underline{https://www.uwgb.edu/dutchs/Petrology/MolybdeniteStructure.HTM}$

Carbonate Minerals



calcite	CaCO ₃	hexagonal	2.71 g/cm ³
aragonite	CaCO ₃	orthorhombic	2.94 g/cm ³
magnesite	MgCO_3	source of Mg	

dolomite	CaMg(CO ₃) ₂	source of Mg	
siderite	FeCO ₃		
rhodochrosite	$MnCO_3$	source of Mn	



 $\underline{https://commons.wikimedia.org/wiki/File:Calcite.GIF}$

calcite structure is similar to ${}^{VI}X_2O_3$ **group**, with the oxygen in approximately hexagonal closest packing and the Ca cations in 1/3 of the 'holes'

Sulfate Minerals

evaporites

gypsum	^{VIII} CaSO ₄ ⋅ 2H ₂ O		wallboard
anhydrite	VIIICaSO ₄	orthorhombic	
barite	XIIBaSO ₄		source of Ba





gypsum

anhydrite

Phosphate Minerals

apatite	$\operatorname{Ca}_{5}(\operatorname{PO}_{4})_{3}(\operatorname{OH},\operatorname{Cl},\operatorname{F})$	hexagonal	source of P
monazite	Ce(PO ₄)	monoclinic	source of P



Ce(PO₄)

source of Th

Tungstate Minerals

scheelite	CaW ⁶⁺ O ₄	source of W
-----------	----------------------------------	-------------



(from

 $\underline{http://www.wrightsrockshop.com/gallery/wulfenitemimetite/wulfenitemimetitemiscellaimages/scheelite022504.JPG)}$

Borate Minerals

borax hydrous Na borate (including borax, colemanite, kernite, ulexite) source of B

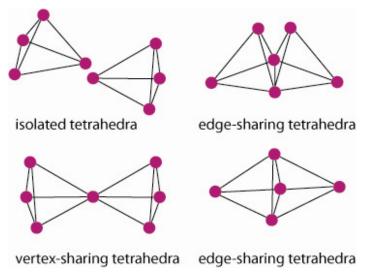


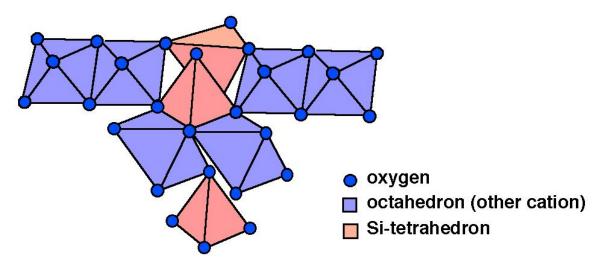
Silicate Minerals

		no of O shared
type	-silicate	between tetrahedra
orthosilicates	neso	0
disilicates	soro	1
ring silicates	cyclo	2
chain silicates	ino	2 or 3
sheet silicates	phyllo	3
framework silicates	tecto	4

Pauling's Rule 3

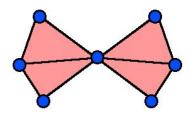
two cations prefer to share one anion (e.g., Si-O-Si), rather than two (which creates a polyhedra/polyhedra edge), and definitely rather than three (which creates a polyhedra/polyhedra face)





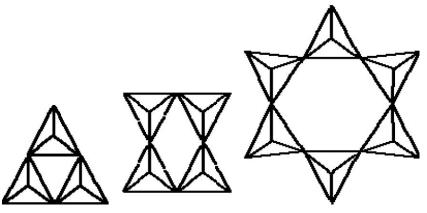
nesosilicate isolated tetrahedra (from

http://classes.colgate.edu/rapril/geol201/summaries/silicates/neso.htm)



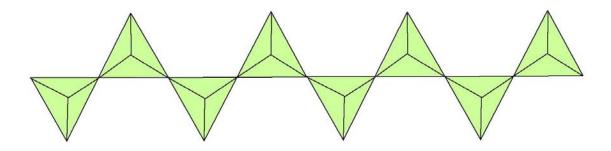
sorosilicate tetrahedra pairs/sisters (from

http://classes.colgate.edu/rapril/geol201/summaries/silicates/soro.htm)



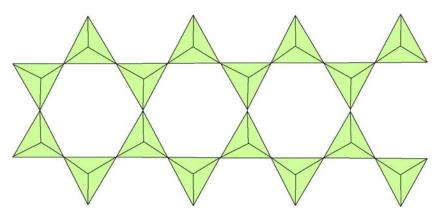
cyclosilicate share 2 oxygen per tetrahedron (from

http://classes.colgate.edu/rapril/geol201/summaries/silicates/cyclo.htm)



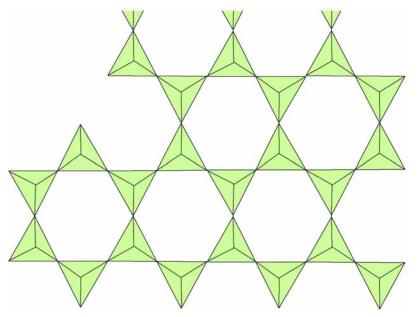
single-chain inosilicate share 2 oxygen per tetrahedron (from

http://classes.colgate.edu/rapril/geol201/summaries/silicates/ino.htm)



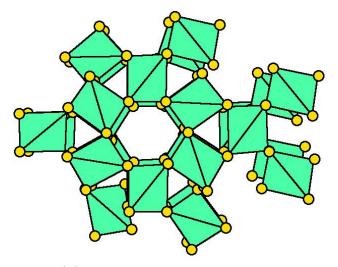
double-chain inosilicate share 2-3 oxygen per tetrahedron (from

http://classes.colgate.edu/rapril/geol201/summaries/silicates/amphib.htm)



phyllosilicate share 3 oxygen per tetrahedron (from

http://classes.colgate.edu/rapril/geol201/summaries/silicates/phyllo.htm)



tectosilicate share 4 oxygen per tetrahedron (from

http://classes.colgate.edu/rapril/geol201/summaries/silicates/tecto.htm)

Orthosilicates (Nesosilicates)

 SiO_4 + cations

zircon

ZrSiO₄



 $\underline{http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met_minerals.htm\#Al-silicates)}$

crystal structure movie:

+ http://nature.berkeley.edu/classes/eps2//wisc/geo36o/zircon.mov (SiO₄ tetrahedra blue, Zr⁴⁺ 8-fold sites green)

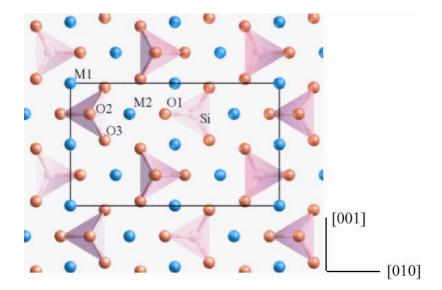
olivine





(from http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met minerals.htm#Al-silicates)

orthorhombic **forsterite** Mg₂SiO₄ in ultramafic rocks **fayalite** Fe₂SiO₄

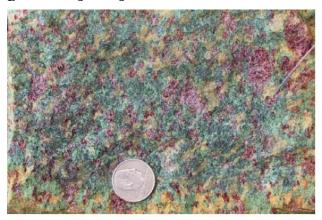


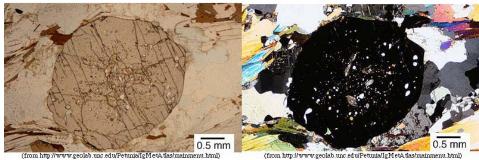
crystal structure movie:

+http://nature.berkeley.edu/classes/eps2//wisc/geo360/olivine.mov

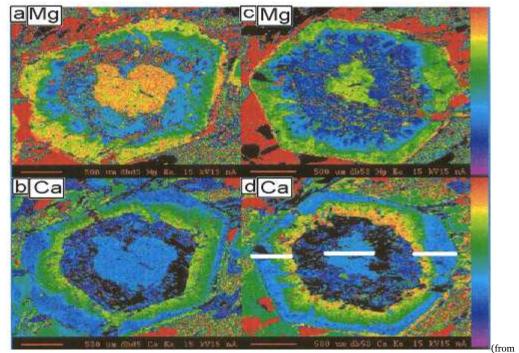
 $(SiO_4$ tetrahedra blue, Fe & Mg distorted octahedral sites yellow, Fe & Mg octahedral sites orange)

$garnet \, X_3Y_2Si_3O_{12}$





almandine Fe pyrope Mg grossular Ca spesssartine Mn Y-garnet $Y_3Al_2Si_3O_{12}$



http://www.geo.uni-potsdam.de/Mitarbeiter/OBrien/obrien/Atoll/index.html)

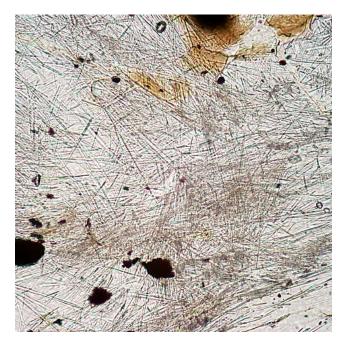
crystal structure movie:

http://nature.berkeley.edu/classes/eps2//wisc/geo36o/garnet.mov (SiO₄ tetrahedra blue, Al octahedra red, M²+ distorted 8-fold sites cyan)

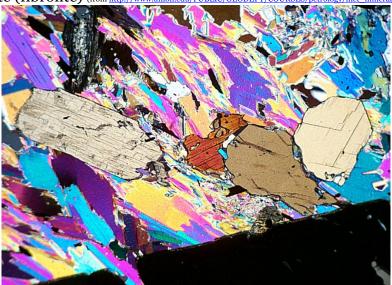
Aluminumsilicates (also orthosilicates)

Al₂SiO₅

sillimanite VIAlIVAl	orthorhombic	high temperature
andalusite VIAlVAl	orthorhombic	low pressure
kyanite ^{VI} Al ^{VI} Al	triclinic	high pressure

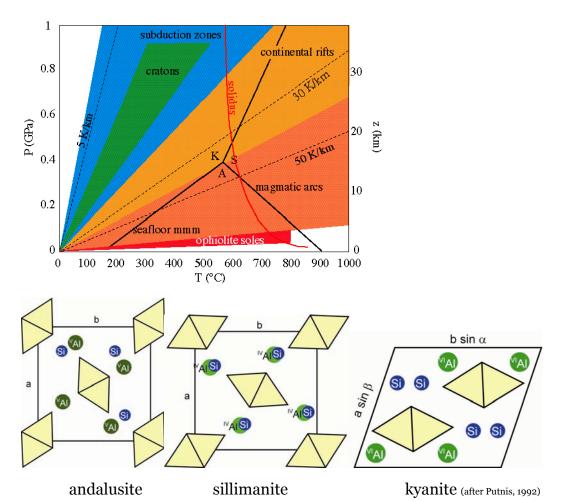


 $sillimanite \ (fibrolite) \ {\it (from $\underline{\tt http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met_minerals.htm\#Al-silicates)} \\$



 $ky an ite \ {\it (from $http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met_minerals.htm\#Al-silicates)}$



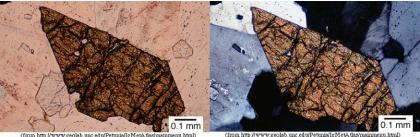


crystal structure movies:

<u>http://nature.berkeley.edu/classes/eps2//wisc/geo360/andalusite.mov</u> (SiO₄ tetrahedra blue, ^{VI}Al pale blue, ^VAl green)

 $\frac{\text{http://nature.berkeley.edu/classes/eps2//wisc/geo360/sillimanite.mov}}{\text{tetrahedra blue, }^{VI}\text{Al pale blue, }^{IV}\text{Al yellow)}} (SiO_4$

<u>ti</u>tanite



(from http://www.geolab.unc.edwPetunia/IgMetA CaTiSiO4(OH,Cl,F)4

staurolite





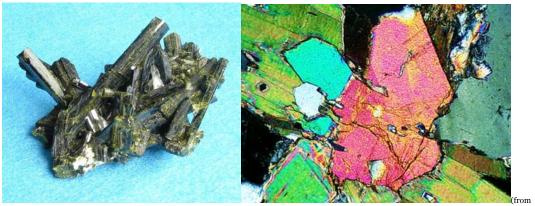
 $\frac{\text{(from $\underline{\text{http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met_minerals.htm#Al-silicates)}}$

(Mg,Fe)₂Al₉Si₄O₂₂(OH)₂

Disilicates (Sorosilicates)

paired SiO_4 tetrahedra, Si_2O_7 (Si_2O_8 with each tetrahedron sharing one O with one other tetrahedron)

epidote Ca₂(Al,Fe⁺³)Al₂Si₃O₁₂(OH)



http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met minerals.htm#Al-silicates

monoclinic

has 7 and 11-fold coordinated sites structure movie:

+http://nature.berkeley.edu/classes/eps2//wisc/geo360/epidote.mov (Ca 7- and 11-fold sites green, Si tetrahedra chains blue, Al M2 octahedral site cyan, Al-Fe M1 octahedral site yellow)

zoisite Ca₂Al₃Si₃O₁₂(OH) orthorhombic

lawsonite CaAl₂Si₂O₇(OH)₂·H₂O indicates high pressure

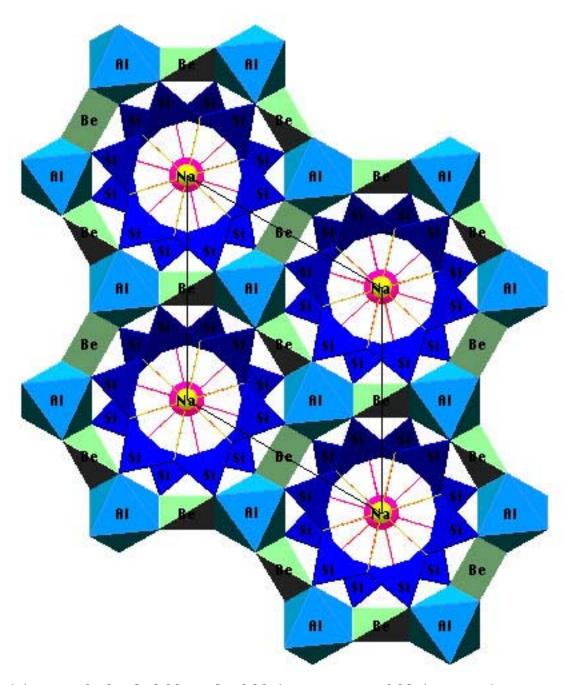
Ring Silicates (Cyclosilicates)

six-fold rings of SiO_4 tetrahedra, Si_6O_{18} (Si_6O_{24} with each tetrahedron sharing two O with two other tetrahedra)

beryl Be₃Al₂Si₆O₁₈

hexagonal





(SiO4 tetrahedra dark blue, Al 6-fold sites cyan, Be 4-fold sites green) crystal structure movie: +

+http://nature.berkeley.edu/classes/eps2//wisc/geo360/beryl.mov (SiO4 tetrahedra blue, Al 6-fold sites green, Be 4-fold sites pale green; ignore the yellow and pink)

(cordierite structure nearly the same)

tourmaline Li-B silicate

Na(Mg,Fe,Mn,Li,Al)₃Al₆Si₆O₁₈(BO₃)₃(OH)₄

crystal structure movie:

http://nature.berkeley.edu/classes/eps2//wisc/geo360/tourmaline.mov (SiO₄ tetrahedra cyan, Na⁺ or OH⁻ yellow, Al cyan, Li & Mg and Al purple, BO₃ pale green)

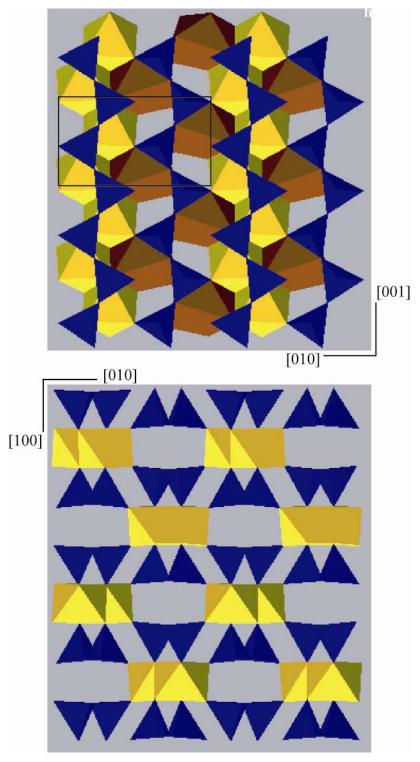


http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met_minerals.htm#Al-silicates

Chain Silicates (Inosilicates)

Pyroxene

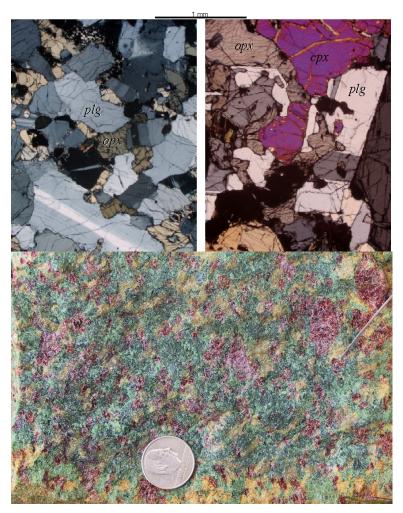
single chains of SiO_4 tetrahedra, Si_2O_6 (Si_2O_8 with each tetrahedron sharing two O with two other tetrahedra)



 $+ \underline{http://nature.berkeley.edu/classes/eps2//wisc/geo360/opx.mov} \hspace{0.1cm} \textbf{(SiO_4)}$

tetrahedra blue, Mg & Ca octahedra yellow)

http://nature.berkeley.edu/classes/eps2//wisc/geo360/diopside.mov (SiO4 tetrahedra blue, Mg octahedra yellow, Ca octahedra orange)



orthorhombic and monoclinic \$\$^{VIII\ or\ VI}X^{VI}Y^{IV}Z_2O_6\$\$\$^{VIII\ or\ VI}M2^{VI}M1^{IV}T_2O_6\$\$\$

enstatite

 $MgSiO_3$

ferrosilite

 $FeSiO_3$

wollastonite

 $CaSiO_3$ common in skarns



diopside

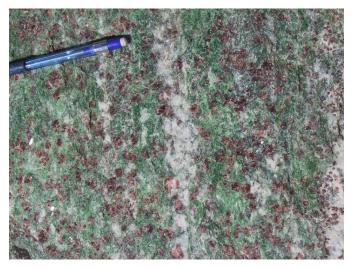
 $CaMgSi_{2}O_{6} \\$

hedenbergite

 $CaFeMgSi_{2}O_{6} \\$

jadeite

 $NaAlSi_2O_6$ indicates high pressure



augite

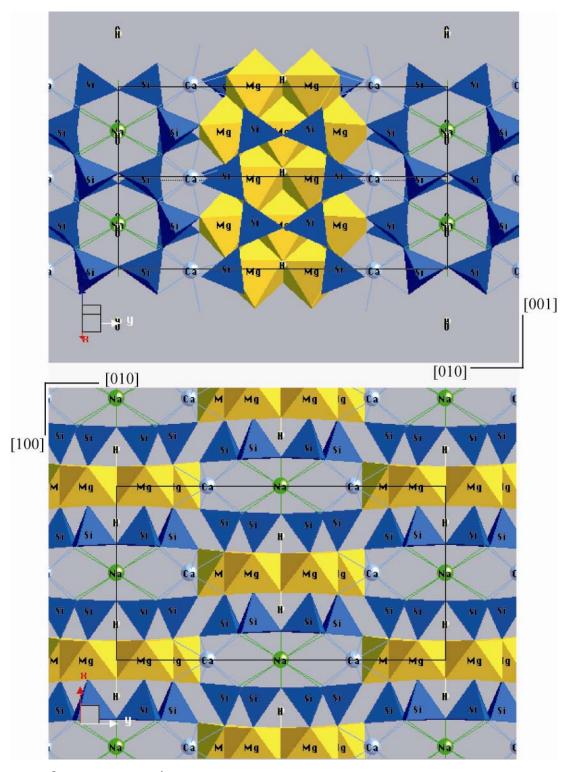
 $(Na,Ca,Fe,Mg)(Al,Ti,Si)_2O_6$

Amphibole

double chains of SiO_4 tetrahedra, Si_8O_{22} (Si_8O_{32} with each tetrahedron sharing two or three O with other tetrahedra) orthorhombic and monoclinic

$${}^{\mathrm{X}}W_{0-1}{}^{\mathrm{VIII}\,\mathrm{or}\,\mathrm{VI}}X_{2}{}^{\mathrm{VI}}Y_{5}{}^{\mathrm{IV}}Z_{8}O_{22}(OH)_{2}$$

$${}^{X}A_{0-1}{}^{VIII\; or\; VI}M4_{2}{}^{VI}(M1,\, M2,\, M3)_{5}{}^{IV}T_{8}O_{22}(OH)_{2}$$



crystal structure movies:

+<u>http://nature.berkeley.edu/classes/eps2//wisc/geo360/tremolite.mov</u> (SiO4 tetrahedra blue, Mg octahedra yellow, Ca 8- or 6-fold sites pale blue, Na 10-fold site green) http://ist-

http://nature.berkeley.edu/classes/eps2//wisc/geo360/glaucophane.mov
(SiO4 tetrahedra blue, Mg octahedra yellow, Al 8- or 6-fold sites pale blue, Na 10-fold site green)

anthophyllite []Mg₂Mg₅Si₈O₂₂(OH)₂

Mg-Fe orthoamphibole Mg-rich rocks: ultramafic



$tremolite-actinolite \cite{Ca_2Mg_5Si_8O_{22}(OH)_2}$

Ca-Mg-Fe clinoamphibole tremolite is Mg endmember; skarns actinolite is Fe endmember; blackwall rinds



glaucophane []Na₂(Mg₃Al₂)Si₈O₂₂(OH)₂

Na clinoamphibole

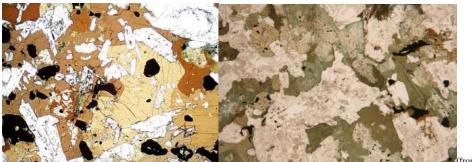
indicates high pressure



 $\underline{http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met_minerals.htm\#Al-petrology/met_minerals.htm$

hornblende (Na, K)Ca₂(Mg, Fe²⁺, Fe³⁺, Al, Ti)₅Si₈O₂₂(OH)₂

K, Na, K, Mg, Fe, Al clinoamphibole

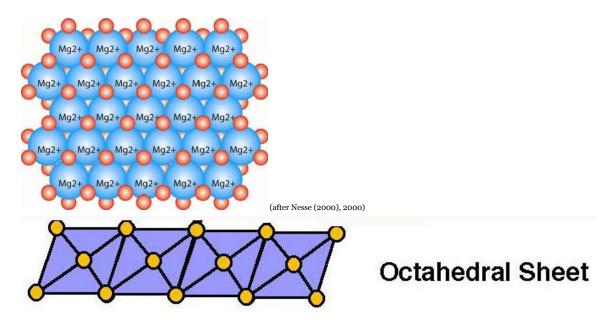


http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met_minerals.htm#Al-silicates

Sheet Silicates (Phyllosilicates)

brucite: Mg(OH)₂

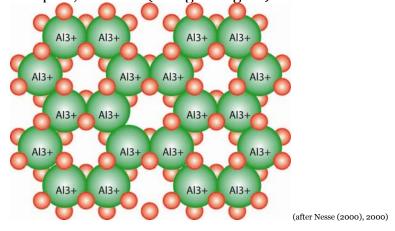
Mg atoms sit in octahedral sites between two planes of OH; the resulting Mg(OH)₂ sheets are held together by van der Waals bonds the 6– charge of the anions is satisfied by three 2+ cations, so no sites are vacant, leading to a tri-octahedral sheet in which all 3 of the octahedral sites are occupied; each OH (orange in figure) is bonded to three Mg²⁺



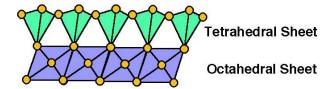
gibbsite: Al(OH)₃

Al atoms sit in octahedral sites between two planes of OH; the resulting $Al(OH)_3$ OH sheets are held together by van der Waals bonds

the 6– charge of the anions is satisfied by two 3+ cations, so 1/3 of the sites are vacant, leading to a di-octahedral sheet in which 2/3 of the octahedral sites are occupied; each OH (orange in figure) is bonded to two Al³⁺



serpentine: Mg₃Si₂O₅(OH)₄

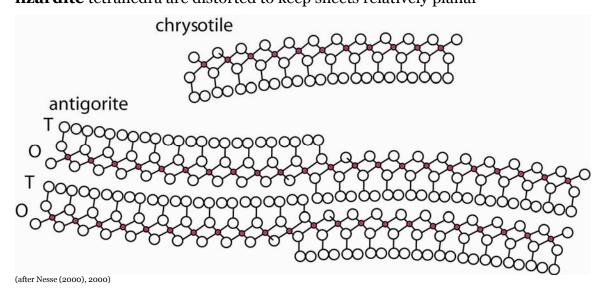


(from http://classes.colgate.edu/rapril/geol201/summaries/silicates/phyllo.htm)

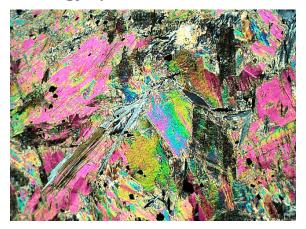
'TO' structure composed of 'brucite', Mg(OH)₂ octahedral layers, and Si₂O₅ tetrahedral sheets

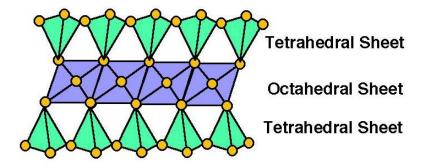
there is a mismatch between the octahedral and tetrahedral layers, which is 'solved' by the various polymorphs of serpentine in different ways: **chrysotile** crystals form rolls parallel to [100] (asbestos)

antigorite tetrahedra positions change to keep sheets relatively planarlizardite tetrahedra are distorted to keep sheets relatively planar



talc: Mg₃Si₄O₁₀(OH)₂





(from http://classes.colgate.edu/rapril/geol201/summaries/silicates/phyllo.htm)

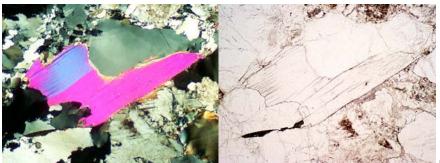
TOT structure, composed of two tetrahedral sheets of Si_2O_5 and an octahedral sheet of $Mg(OH)_2$; successive TOT layers are held together by van der Waals bonds

crystal structure movie:

+http://nature.berkeley.edu/classes/eps2//wisc/geo360/talc.mov

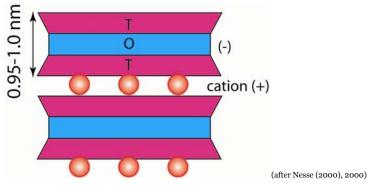
muscovite: KAl₂(AlSi₃O₁₀)(OH)₂ lepidolite: LiAl₂(AlSi₃O₁₀)(OH)₂





http://www.union.edu/PUBLIC/GEODEPT/COURSES/petrology/met_minerals.htm#Al-silicates)

TOT + interlayer cation

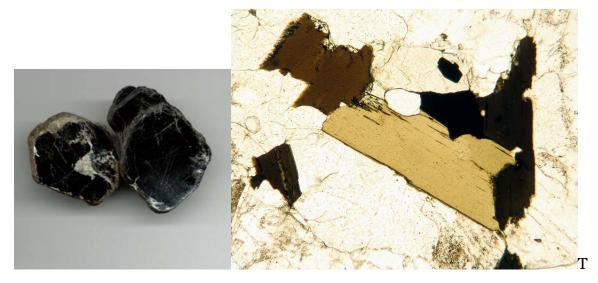


crystal structure movie:

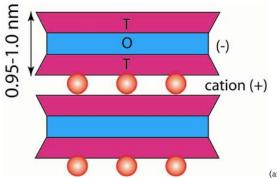
 $+ \underline{\text{http://nature.berkeley.edu/classes/eps2//wisc/geo36o/muscovite.mov}}$

biotite: K(Mg, Fe)₃(AlSi₃O₁₀)(OH)₂

phlogopite is Mg endmember; found in mantle



OT + interlayer cation like muscovite



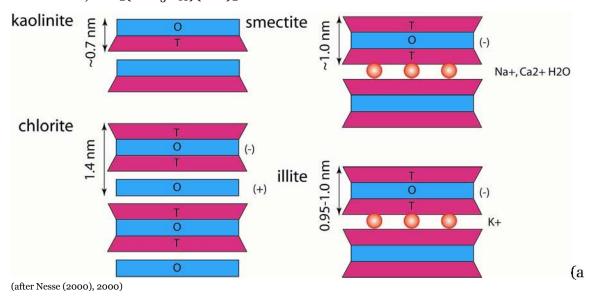
(after Nesse (2000), 2000)

crystal structure movie:

http://nature.berkeley.edu/classes/eps2//wisc/geo360/phlogopite.mov

clay minerals

paper, drilling mud, ceramics, cosmetics, absorbents, food **kaolinite** TO, $Al_2Si_2O_5(OH)_4$, interlayer spacing ~0.7 nm **smectite** TOT, (Na, Ca, Mg, Fe)_x(Si, Al)₄O₁₀(OH)₂ · nH₂O **illite** TOT, $KAl_2(AlSi_3O_{10})(OH)_2$



http://nature.berkeley.edu/classes/eps2//wisc/geo360/kaolinite.mov

chlorite: (Mg, Fe)₃(Al, Si)₄O₁₀(OH)₂

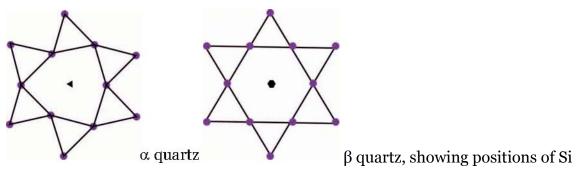
TOT + interlayer octahedral site = talc + brucite crystal structure movie:

http://nature.berkeley.edu/classes/eps2//wisc/geo360/chlorite.mov



Framework Silicates (Tectosilicates)

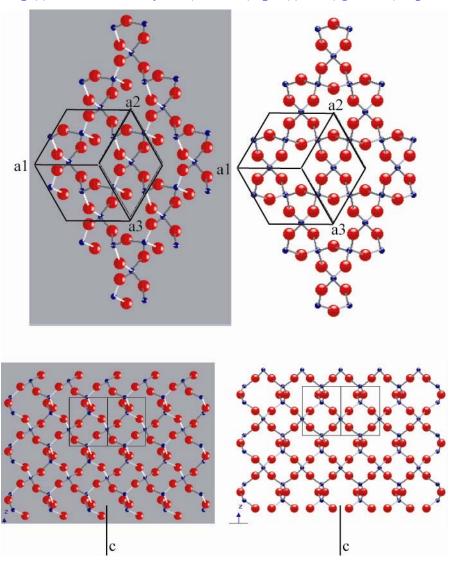
Quartz



atoms (after Putnis, 1992)

+http://nature.berkeley.edu/classes/eps2//wisc/geo360/Quartz.mov

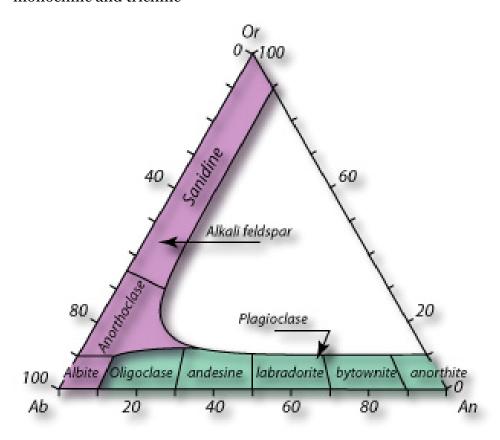
http://nature.berkeley.edu/classes/eps2//wisc/geo360/Bquartz.mov



Feldspar



monoclinic and triclinic



 $\underline{http://www.geosci.usyd.edu.au/users/prey/FieldTrips/SouthCoastExcuo2/DayThree.html}$

$K\text{-}feldspar\ KAlSi_3O_8$

crystal structure movie:

http://nature.berkeley.edu/classes/eps2//wisc/geo360/Sanidine.mov (SiO4 and AlO4 tetrahedra blue, 9-fold K sites red)

sanidine	monoclinic	high T, rapid	complete Al/Si
		cooling	disorder
orthoclase	monoclinic	moderate T,	partial Al/Si
		cooling	disorder
microcline	triclinic	low T, slow	complete Al/Si
		cooling	order





 $plagio clase\ NaAlSi_3O_8-CaAl_2Si_2O_8$



amazonite (albite)

high albite	triclinic	high T, rapid	complete Al/Si
		cooling	disorder
intermediate	triclinic	moderate T,	partial Al/Si
albite		cooling	disorder
low albite	triclinic	low T, slow	complete Al/Si
		cooling	order

crystal structure movie:

+http://nature.berkeley.edu/classes/eps2//wisc/geo360/Albitem.mov

(SiO₄ and AlO₄ tetrahedra blue, Na 9-fold sites yellow)

this is the best of the feldspar movies

http://nature.berkeley.edu/classes/eps2//wisc/geo360/Anorthite.mov

 $(SiO_4 \, tetrahedra \, blue, \, AlO_4 \, tetrahedra \, grey, \, Ca \, 9$ -fold sites blue)

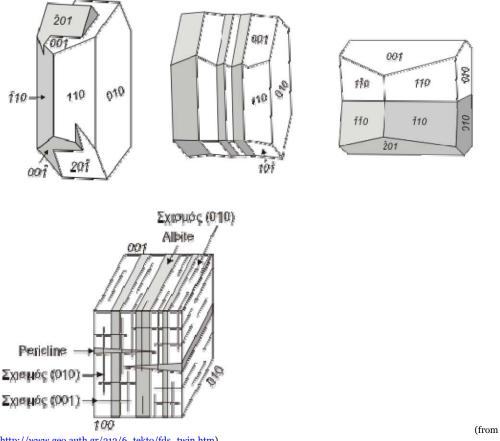
albite-anorthite

albite-An 10-oligo clase-An 30-ande sine-An 50-labradorite-An 70-bytown ite-An 90-an orthite





feldspar twinning



http://www.geo.auth.gr/212/6 tekto/fds twin.htm)

Albite \(^(010)(010)\)

Pericline [010](hol)

Albite and Pericline

Carlsbad [001](010)

Zeolites

'(Na, K)(Ca, Mg)(AlSiO)'·mH₂O

important filtering agents crystal structure movie:

+http://nature.berkeley.edu/classes/eps2//wisc/geo360/Analcime.mov (SiO4 & AlO₄ tetrahedra purple, Na pink, H₂O yellow)

Igneous Petrology

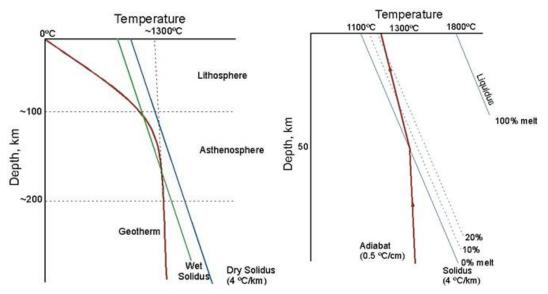
Read Chapters 8 & 9 of Klein & Philpotts

Mid-Ocean Ridge Magmatism

Earth's is differentiated into core, mantle crust.

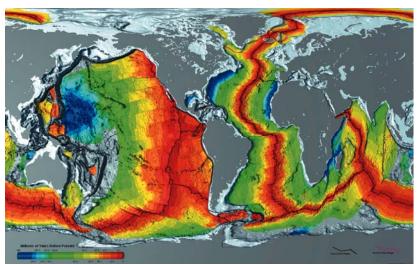
Mantle is undergoing convection because of core crystallization, radiogenic heat etc.

Peridotite is made of olivine + clinopyroxene + orthopyroxene On the rising part of a convection cell, decompression melting occurs



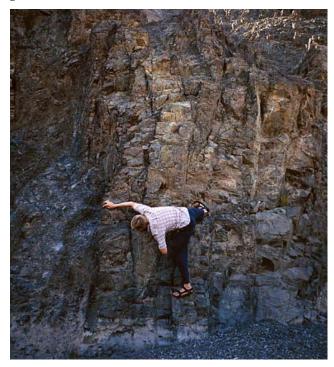
http://gore.ocean.washington.edu/classpages/ocean410 2001/notes/unito5.htm

This melting is incongruent and depletes the clinopyroxene component in peridotite, producing basalt (MORB) that erupts at the seafloor at mid-ocean ridges and diabase dikes and gabbro that crystallize beneath the seafloor.





pillowed flows in Oman

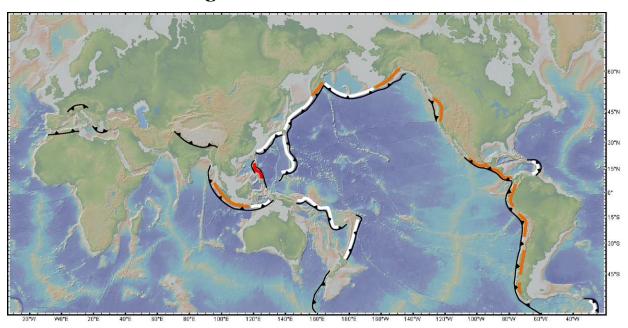


sheeted dikes in Oman



gabbro in Oman

Subduction Zone Magmatism



 $\underline{http://geosphere.geoscienceworld.org/content/9/1/21/F4.expansion.html}$

Oceanic lithosphere undergoes hydration during and after formation.

Oceanic lithosphere cools, eventually becoming gravitationally
unstable and subducting

During subduction, the downgoing plate heats and devolatilizes.

The volatiles migrate upward and trigger melting of the convecting mantle wedge at ~ 1000 °C.

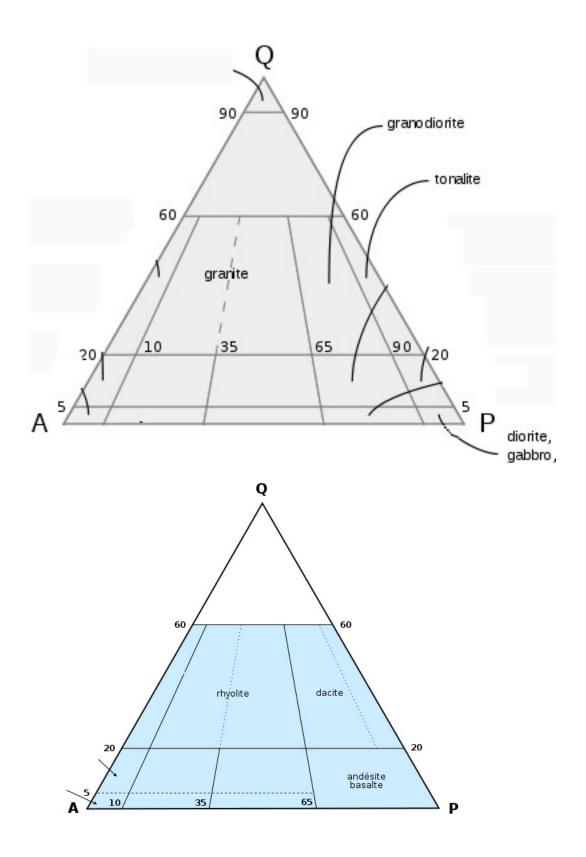
The main magma is basalt. This basalt undergoes differentiation/fractionation and assimilation/contamination to produce more-felsic rocks; more-felsic rocks can also be produced by re-melting of crustal rocks.

Plutonic rocks form batholiths.

In intra-oceanic arcs, these processes produce basalt = andesite >> dacite, rhyolite.

In continental arcs, processing is more severe, leading to andesite > dacite > basalt >rhyolite.

More-felsic rocks have higher SiO₂, H₂O and viscosity (and are therefore more explosive).



Metamorphic Petrology

Read Chapters 8 & 9 of Klein & Philpotts

The main metamorphic facies are greenschist (albite + actinolite + epidote + chlorite), amphibolite (plagioclase + hornblende), granulite (plagioclase + clinopyroxene + orthopyroxene), blueschist (Na-amphibole + epidote or lawsonite), and eclogite (Na-clinopyroxene + garnet).

Oceanic crust undergoes low-P/high-T metamorphism at mid-ocean ridges. Subducting oceanic crust transforms to blueschist and eclogite during high-P/low-T metamorphism; the volatiles produced migrate into the mantle wedge and cause melting. Eclogite is substantially denser than peridotite, and produces about half of the negative buoyancy of subducting plates.

Barrovian metamorphic rocks are produced during continental collision. The sequence of minerals that appear during Barrovian metamorphism is chlorite, biotite, garnet, staurolite, kyanite, sillimanite, sillimanite + orthoclase.