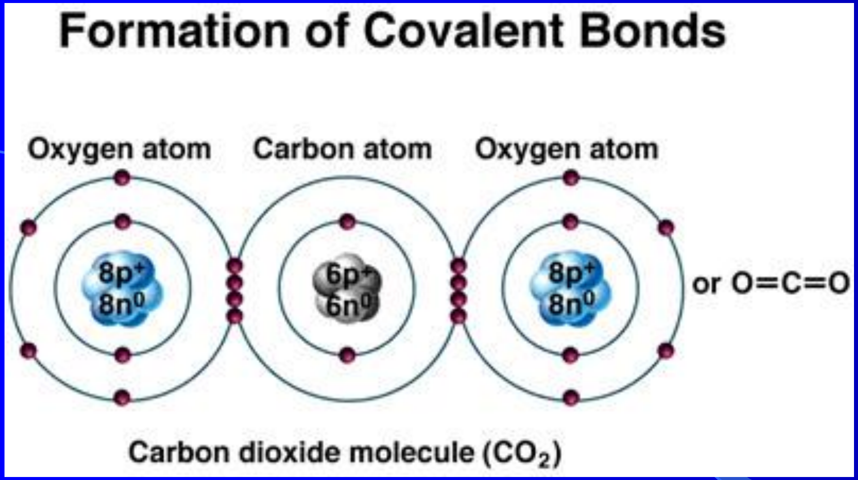
Earth Materials II

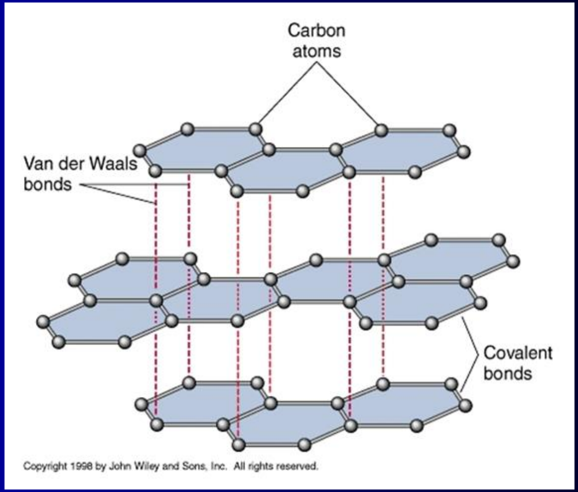
Review - Crystal Structures & Symmetry

Definition of a mineral

- Naturally occurring
- Characteristic internal structure
- Chemical composition either fixed or varies within certain limits (solid solution minerals)

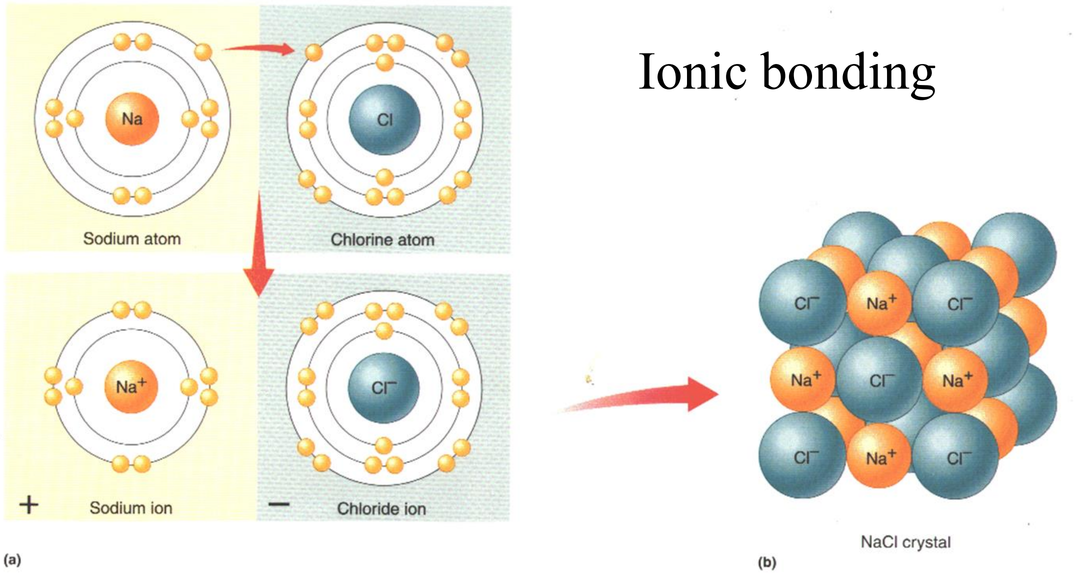
Types of Bonding

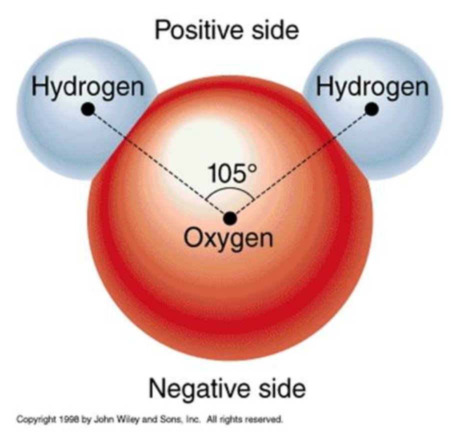




Van der Waals bonding

Ionic bonding





Hydrogen bonding

Table 7-2. Electronegativities

Z	Ion	Electro-negativity	Z	Ion	Electro-negativity	Z	Ion	Electro-negativity
1	H^+	2.20	33	As^{5+}	2.18	65	Dy^{3+}	1.22
3	Li^+	0.98	34	Se^{2-}	2.55	67	Ho^{3+}	1.23
4	Be^{2+}	1.57	35	Br^-	2.96	68	Er^{3+}	1.24
5	B^{3+}	2.04	37	Rb^+	0.82	69	Tm^{3+}	1.25
6	C^{4+}	2.55	38	Sr^{2+}	0.95	70	Yb^{3+}	---
7	N^{5+}	3.04	39	Y^{3+}	1.22	71	Lu^{3+}	1.0
8	O^{2-}	3.44	40	Zr^{4+}	1.33	72	Hf^{4+}	1.3
9	F^-	3.98	41	Nb^{5+}	1.6	73	Ta^{5+}	1.5
11	Na^+	0.93	42	Mo^{6+}	2.16	74	W^{6+}	1.7
12	Mg^{2+}	1.31	43	Tc^{2+}	2.10	75	Re^{7+}	1.9
13	Al^{3+}	1.61	44	Ru^{2+}	2.2	76	Os^{6+}	2.2
14	Si^{4+}	1.90	45	Rh^{2+}	2.28	77	Ir^{6+}	2.2
15	P^{5+}	2.19	46	Pd^{2+}	2.20	78	Pt^{4+}	2.2
16	S^{2-}	2.58	47	Ag^+	1.93	79	Au^+	2.4
17	Cl^-	3.16	48	Cd^{2+}	1.69	80	Hg^{2+}	1.9
19	K^+	0.82	49	In^{3+}	1.78	81	Tl^{3+}	1.8
20	Ca^{2+}	1.00	50	Sn^{2+}	1.96	82	Pb^{2+}	1.8
21	Sc^{3+}	1.36	51	Sb^{5+}	2.05	83	Bi^{3+}	1.9
22	Ti^{4+}	1.54	52	Te^{2-}	2.1	84	Po^{4+}	2.0
23	V^{3+}	1.63	53	I^-	2.66	85	At^{5+}	2.2
24	Cr^{3+}	1.66	55	Cs^+	0.79	87	Fr^+	0.7
25	Mn^{2+}	1.55	56	Ba^{2+}	0.89	88	Ra^{2+}	0.9
26	Fe^{2+}	1.83	57	La^{3+}	1.10	89	Ac^{3+}	1.1
27	Co^{2+}	1.88	58	Ce^{3+}	1.12	90	Th^{4+}	1.3
28	Ni^{2+}	1.91	59	Pr^{3+}	1.13	91	Pa^{4+}	1.5
29	Cu^+	1.90	60	Nd^{3+}	1.14	92	U^{6+}	1.7
30	Zn^{2+}	1.65	62	Sm^{3+}	1.17	93	Np^{3+}	1.3
31	Ga^{3+}	1.81	64	Gd^{3+}	1.20	94	Pu^{4+}	1.3
32	Ge^{4+}	2.01						

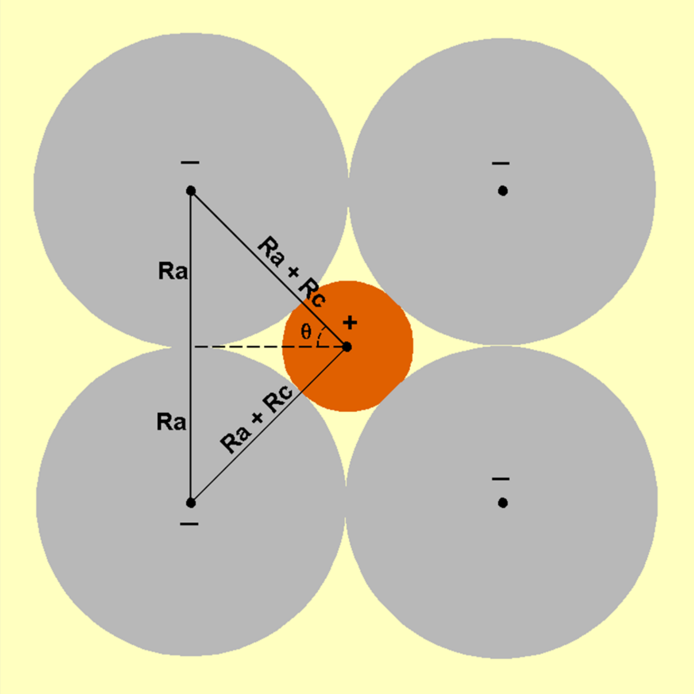
Table 7-3. Percent ionic character of a single chemical bond

Difference in electronegativity	Ionic character, %	Difference in electronegativity	Ionic character, %
0.1	0.5	1.7	51
0.2	1	1.8	55
0.3	2	1.9	59
0.4	4	2.0	63
0.5	6	2.1	67
0.6	9	2.2	70
0.7	12	2.3	74
0.8	15	2.4	76
0.9	19	2.5	79
1.0	22	2.6	82
1.1	26	2.7	84
1.2	30	2.8	86
1.3	34	2.9	88
1.4	39	3.0	89
1.5	43	3.1	91
1.6	47	3.2	92

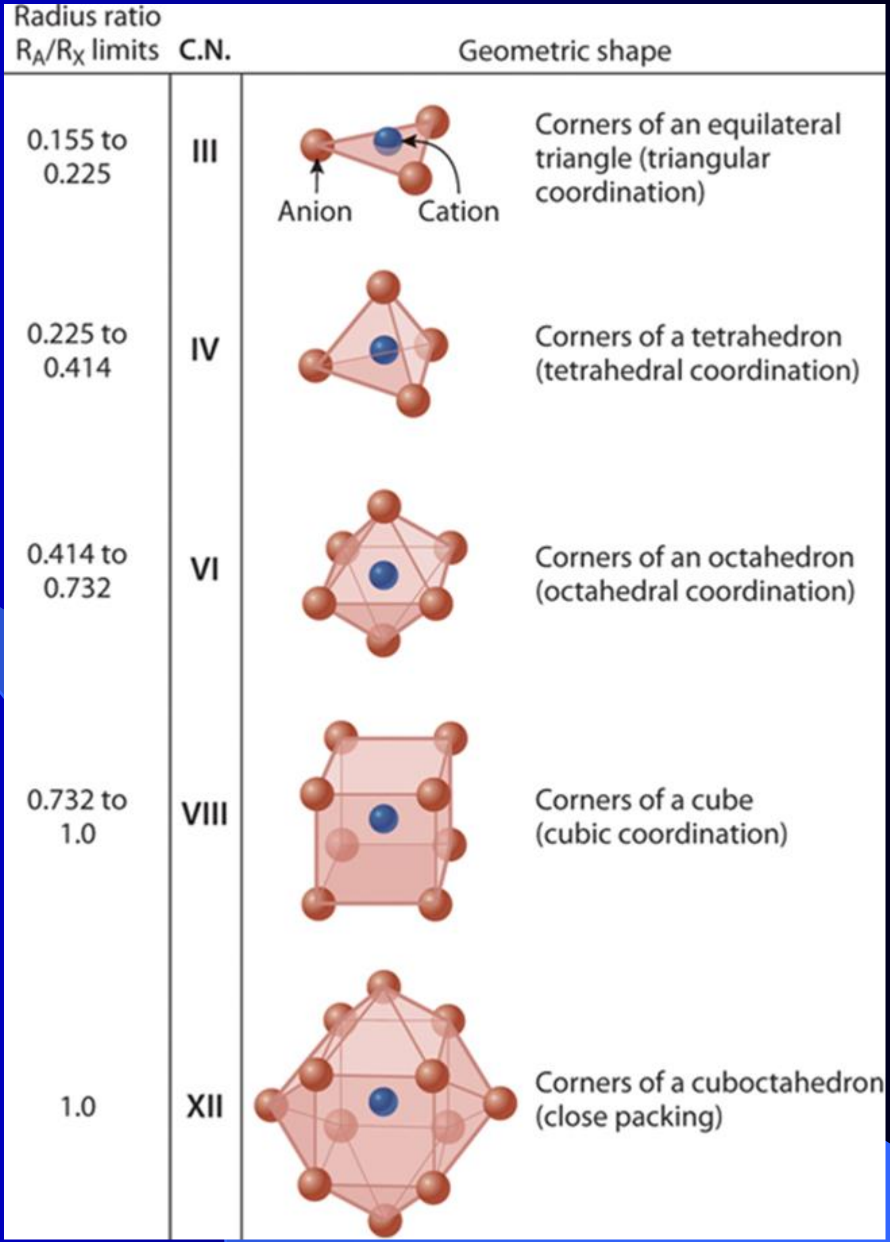
Coordination Principle

Radius Ratio = Radius cation/Radius Anion

This ratio determines how many anions can be packed around a cation.



Packing of anions around a cation for a coordination number of 4. The minimum radius ratio can be calculated from the geometry of the packing. R_a and R_c are the radii of the anion and cation, respectively. In this case, θ = 45°.

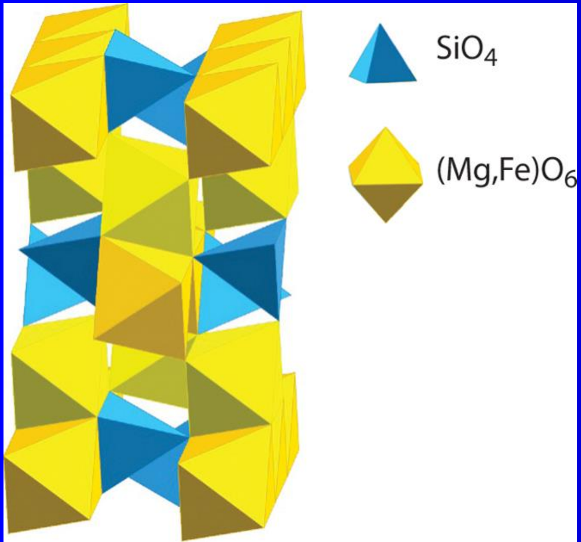


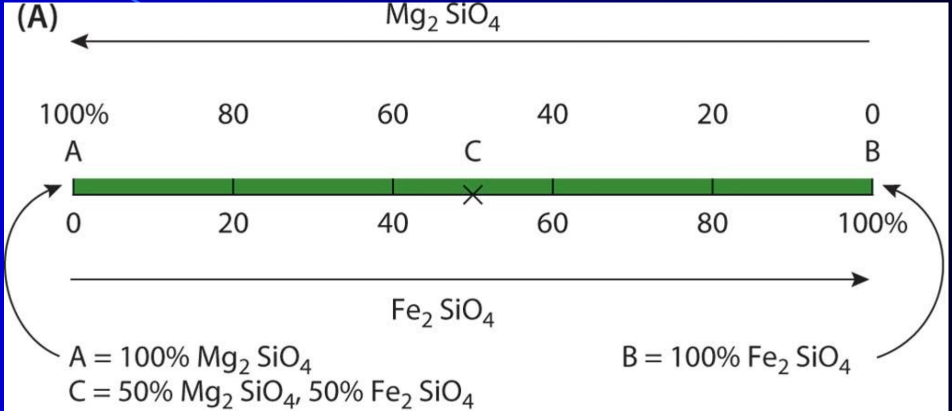
Radius ratio R_A/R_X limits	C.N.	Geometric shape
0.155 to 0.225	III	Corners of an equilateral triangle (triangular coordination)
0.225 to 0.414	IV	Corners of a tetrahedron (tetrahedral coordination)
0.414 to 0.732	VI	Corners of an octahedron (octahedral coordination)
0.732 to 1.0	VIII	Corners of a cube (cubic coordination)
1.0	XII	Corners of a cuboctahedron (close packing)

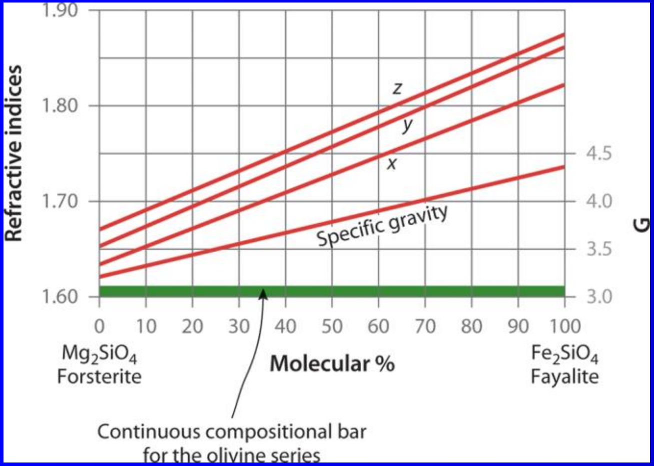
Ionic Substitution

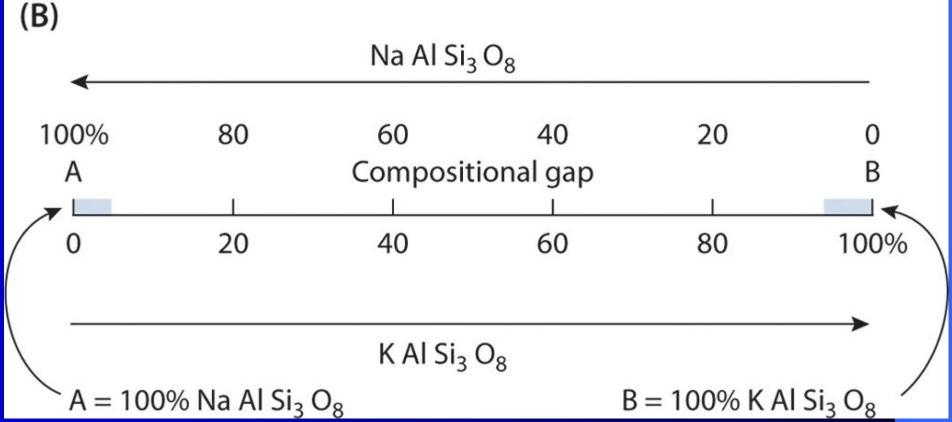
- Ions of one element can substitute for those of another in a crystal structure if their radii differ by less than about 15%
- Ions that differ by one charge unit substitute readily for each other as long as charge neutrality is maintained. Note that this requires a coupled substitution, such as occurs in the plagioclase solid solution series.
- When two ions can occupy the same site in a crystal structure, the ion with the higher ionic potential preferentially enters the site.
- Even if the size and charge of the minor and major ion are similar, substitution may be limited for the minor ion if it has a very different electronegativity and forms a bond of very different character from that of the major ion.

Solid solution series – olivine and feldspar



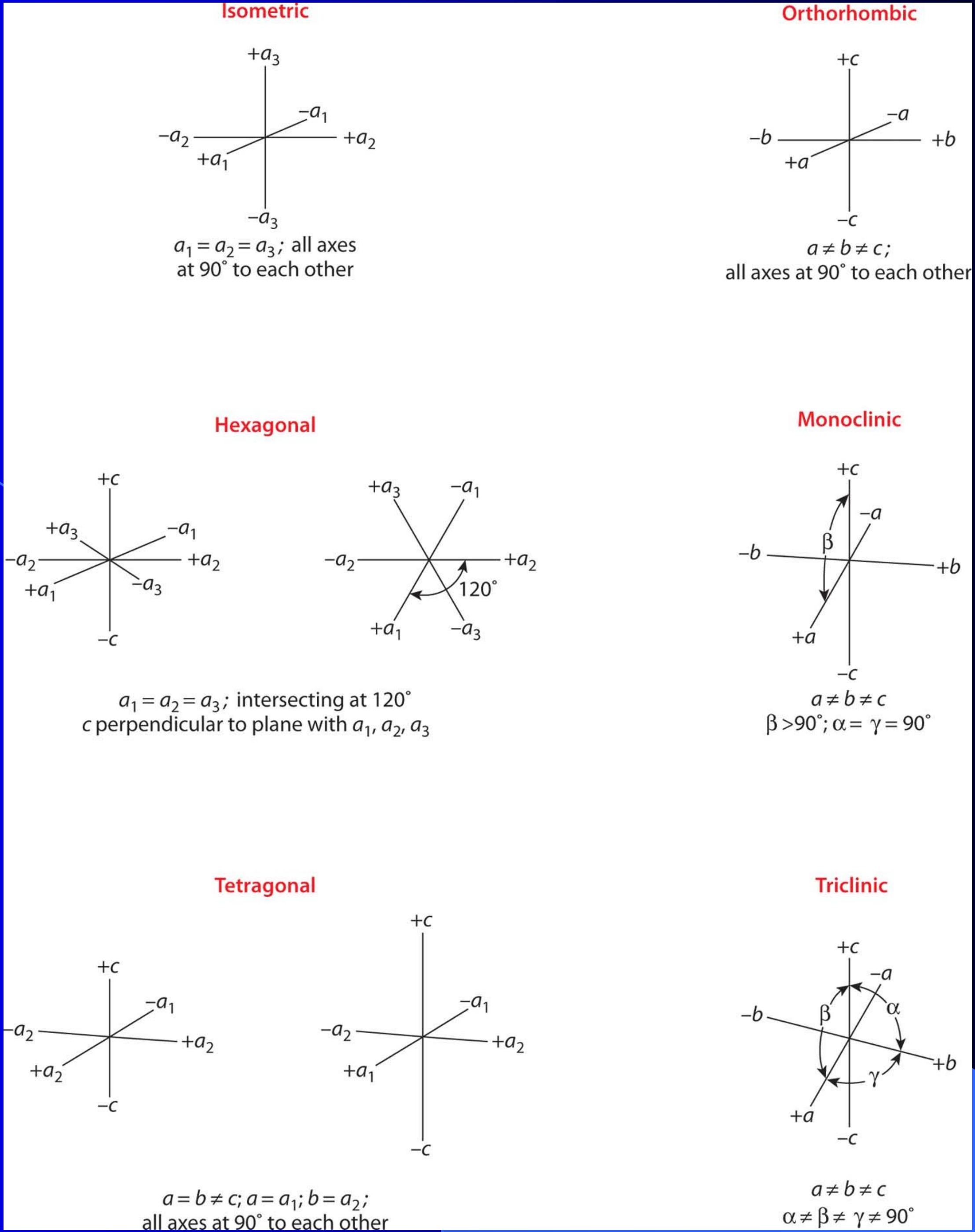






The six crystallographic systems.

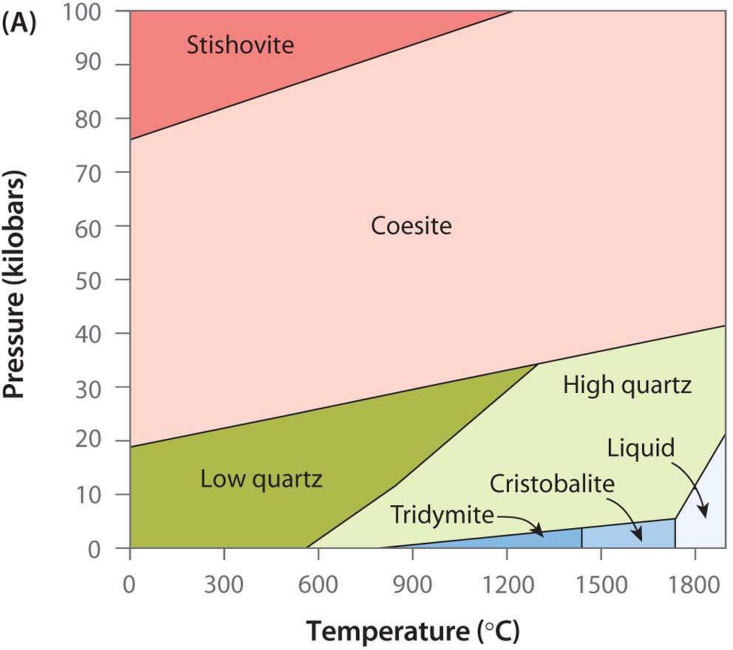
SUPER IMPORTANT

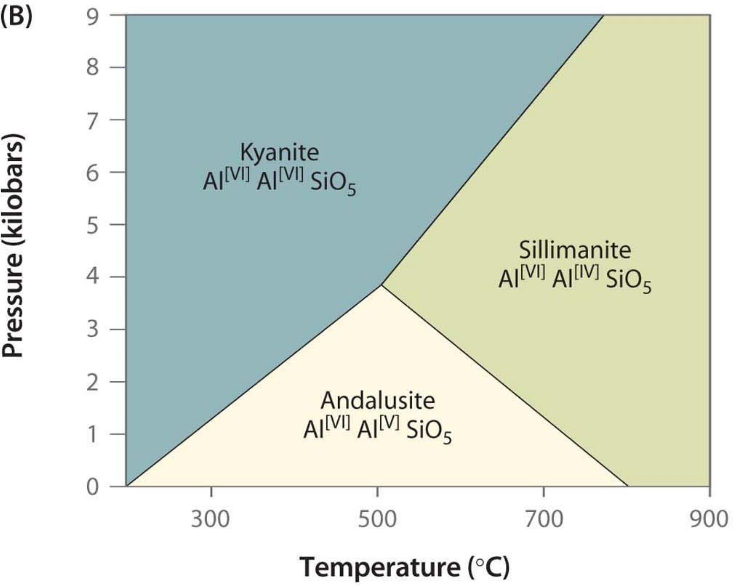


Polymorphism - the ability of a substance to adopt different internal structures and external forms, in response to different conditions of temperature and/or pressure

Types of polymorphism

- **Reconstructive** – extensive rearrangement of the crystal structure involving breaking of bonds and reassembly of structural units into different arrangements.
- **Displacive** – slight rearrangement of crystal structure. No bonds are broken.
- **Order-disorder** – ordering of individual elements in different structural sites in a mineral.
- **Polytypism** – different structural arrangements due to different stacking of sheets in three dimensions (sheet silicates).





Example of order-disorder polymorphism – the polymorphs of $KAlSi_3O_8$.

The distinction between the polymorphs is based on the ordering of Al in the tetrahedral sites.

- Microcline – low T polymorph – one in every four tetrahedral sites is filled with an Al. Total order

- Orthoclase – moderate T polymorph – Al is distributed over two equivalent tetrahedral sites. Partially ordered

- Sanidine – high T polymorph – equal probability of finding Al in any of the four tetrahedral sites. Completely disordered.