Inorganic Chemistry with Doc M.
Fall Semester, 2012
Day 14. Ionic Thrills Part 4.

Name(s):	Element:

Topics:

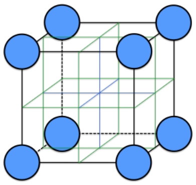
1. Bravis fundamental lattice types

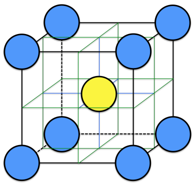
2. Silicates

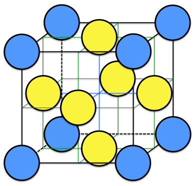
1. Fundamental lattice types.

Bravis determined that almost all natural crystals belong to one of 14 fundamental lattice types. Here we will study these lattices and learn their names.

(a) Cubic unit cells. Cubic unit cells exhibit three equal dimensions along the x, y, and z-axes and three 90° angles. These are the three familiar unit cells, simple cubic, body-centered cubic and face-centered cubic.

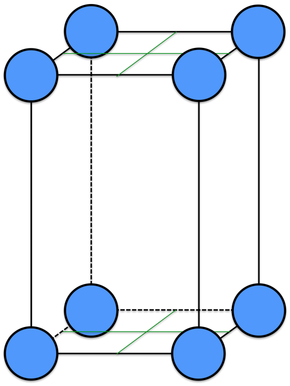






(b) The three cell dimensions are referred to by the symbols ***a***, ***b***, and ***c.*** The angles are those measured between the a and b axes, the a and c axes and between the b and c axes. The angles are referred to by the symbols α, β, and γ. In the case of the cube, we can summarize the relationship of the three axes and three angles to each other as follows: All three, the simple cube, body-centered and face-centered cubes all feature $a = b = c$ and $\alpha = \beta = \gamma = 90^{\circ}$

(b) Tetragonal and Orthorhombic Lattices

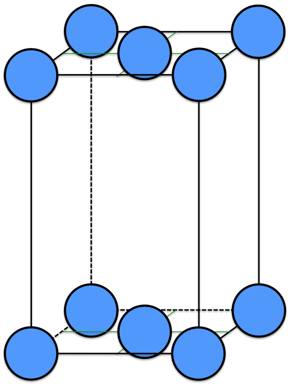


Two simple variations on the cubic lattice are obtained by allowing the cell dimensions to vary from one another but continuing to require three 90° angles. Two possibilities exist: In the simple cube, all three cell dimensions are identical. If we keep two cell dimensions identical and allow the third to be unique, we have produced a ***tetragonal*** unit cell. If all three cell dimensions are unique, we have an ***orthorhombic*** unit cell.

The three possible unit cells in which all angles are 90°

Name	Length of Cell Edge	Angles
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$
Tetragonal	a = b; c is unique	$\alpha = \beta = \gamma = 90^{\circ}$
Orthorhombic	all three unique	$\alpha = \beta = \gamma = 90^{\circ}$

In the Bravis system, the orthorhombic lattice can be modified to form face-centered orthorhombic and body-centered orthorhombic units cells. A fourth important variation exists for orthorhombic unit cell types. Two opposite faces of these unit cells can host a face-centered sphere, while the other four faces are clear. This variation is called the ***base-centered orthorhombic*** unit cell.



Summary of possible unit cells in which all angles are 90^{o}:

Cubic	**Tetragonal**	**Orthorhombic**
1. Simple cubic 2. Face-centered cubic 3. Body-centered cubic	4. Simple tetragonal 5. Body-centered tetragonal	6. Simple orthorhombic 7. Face-centered orthorhombic 8. Body-centered orthorhombic 9. Base-centered orthorhombic

(c) Monoclinic and triclinic lattices

Monoclinic and triclinic unit cells are frequently encountered in nature and chemistry. Each has three unique cell dimensions. Monoclinic unit cells have two 90^{o} angles and one cell angle that is not 90^{o}. Triclinic cells have all three angles unique and not equal to 90^{o}. These parameters are summarized here.

Monoclinic and Triclinic Unit Cell Parameters.

Name	**Length of Cell Edge**	**Angles**
Monoclinic	all three unique	$\alpha = \gamma = 90^{o}$ $\beta < 90^{o}$
Triclinic	all three unique	3 unique angles

Although it would be acceptable to describe monoclinic cells with the angle that is greater than 90^{o}, by convention, most chemists assign the angle to a value less than 90^{o}. So instead of listing the angles for a monoclinic unit cell as 90^{o}, 90^{o}, and 113^{o}, for example, one would customarily list them as 90^{o}, 90^{o}, and 67^{o}.

In the triclinic model, suppose that a chemist measured the three angles to be $\alpha = 102^{o}$; $\beta = 77^{o}$; and $\gamma = 94^{o}$. Convert these angles to standard format.

How many of the eight balls in the triclinic model, actually exhibit all three cell angles to be less than 90^{o}?

Is it possible to have a monoclinic or triclinic unit cell with two cell dimensions exactly the same length? Explain.

In the Bravis system of 14 lattices, the monoclinic unit cell can exhibit a base-centered variation. Thus, we add three more lattices to the list:

Triclinic

10. Simple triclinic

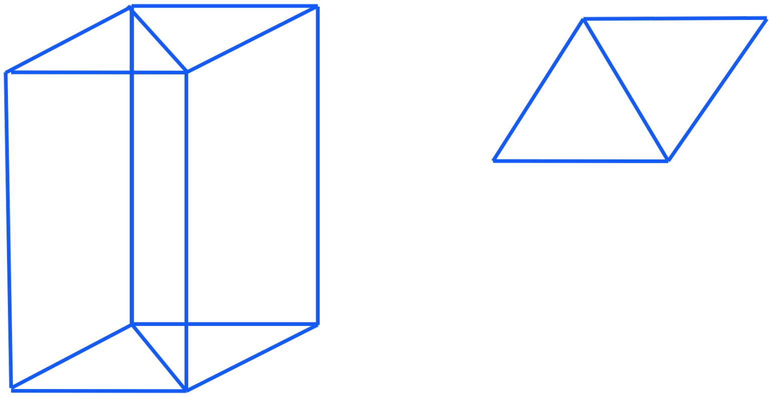
Monoclinic

11. Simple monoclinic
12. Base-centered monoclinic

(d) Hexagonal lattice (includes hcp!)

Hexagonal lattice types are typical in chemistry. Many elements including beryllium, magnesium, cobalt, zinc, cadmium, carbon (graphite) and the elements of the triads of scandium and titanium all exhibit hexagonal close-packed lattices. Cell parameters include two cell angles that are 90^{o} and one that is 60^{o} (120^{o}) as shown below. Hexagonal cell dimensions feature two equal lengths (a = b). Label the cell dimensions and angles in the figure.

Hexagonal unit cell.



(e) Rhombohedral (trigonal) lattices

The rhombohedral unit cell is similar to the simple cubic unit cell in that all three cell dimensions are equal and that all three cell angles are equal. What distinguishes the rhombohedral from the simple cube is that the common angle cannot equal 90°. The rhombohedral lattice is often called the trigonal lattice.

The entire set of Bravis cell types is summarized here.

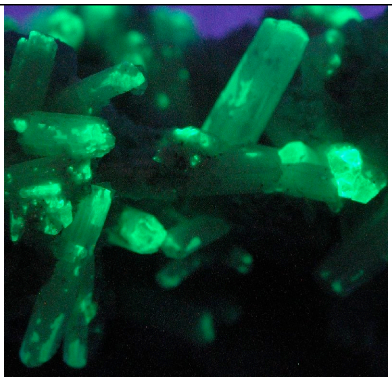
Summary of Fundamental Unit Cell Types.

Name	**Length of Cell Edge**	**Angles**
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$
Tetragonal	$a = b$; c is unique	$\alpha = \beta = \gamma = 90^o$
Orthorhombic	all three unique	$\alpha = \beta = \gamma = 90^o$
Monoclinic	all three unique	$\alpha = \gamma = 90^o$; $\beta < 90^o$
Triclinic	all three unique	3 unique angles; all $< 90^o$
Hexagonal	$a = b$; c is unique	$\alpha = \beta = 90^o$; $\gamma = 60^o$ (120^o)
Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma < 90^o$

2. Silicates.

Silicates are tetrahedral anions in which the silicon atom is bound to four oxygen atoms. Silicates represent a major component of the earth's crust (26% by mass); over 90% of the rocks, minerals, and soils are classified as silicates. Feldspar, which makes up 60% of the crust is a silicate or silicon-oxygen anion. Quartz, mica, talc, basalt, garnet, topaz, zircon, kaolin (clay used to make glossy paper), zeolites and dozens of other less well-known minerals are also all silicates. Silicates can be categorized by structure. Some orthosilicate minerals include:

phenakite, Be_2SiO_4

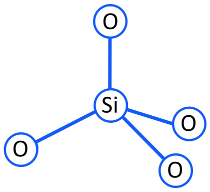


willemite (Zn_2SiO_4)

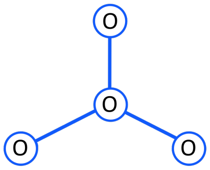
olivine, $(Mg, Fe)_2SiO_4$

 pyrope, $Mg_3Al_2(SiO_4)_3$	 almandine (garnet) ($Fe_3Al_2(SiO_4)_3$)	 grossular, $Ca_3Al_2(SiO_4)_3$
 uvarovite (garnet) ($Ca_3Cr_2(SiO_4)_3$)	 Photo: www.irocks.com, Dr. R. Lavinsky andradite, $Ca_3Fe_2(SiO_4)_3$	 zircon ($ZrSiO_4$)

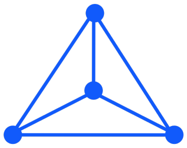
The simplest silicate is the orthosilicate anion, SiO_4^{4-} shown here:



tetrahedral silicate



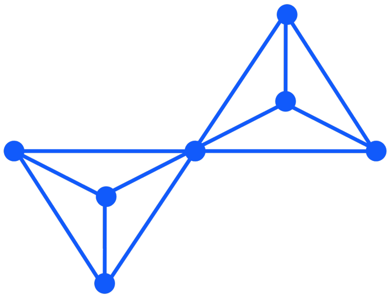
top view
(down O-Si bond)



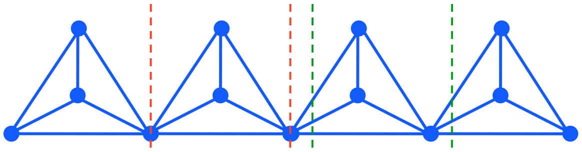
representation
of SiO_4^{4-}

The ball and stick model does not show the fourth oxygen, which occurs directly above or below the silicon, which is centered in a tetrahedron. The line diagram at left gives a shorthand method for representing silicates. The four oxygen atoms that define the tetrahedron are shown. The silicon is located in the center of this tetrahedron and is not shown. You should associate this shape with SiO_4^{4-}.

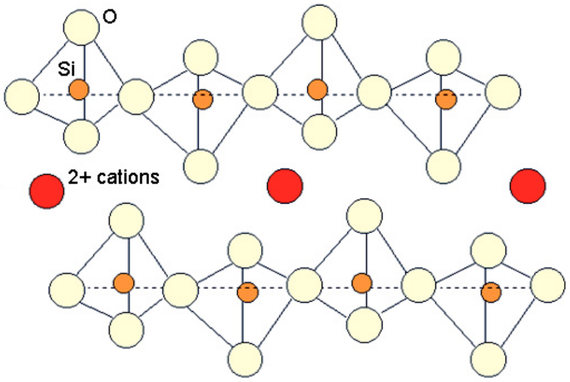
Silicates can become more complex by condensing and sharing an oxygen atom at a corner. This is shown in the figure at left. Here two SiO_4^{4-} units have condensed by sharing an oxide. This amounts to adding two SiO_4^{4-} units and subtracting an O^{2-} unit to give the disilicate anion, $Si_2O_7^{6-}$. Bookkeeping is done by assigning oxidation states of +4 to silicon and -2 to oxygen.



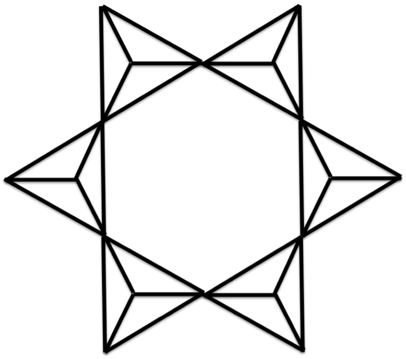
Dental crowns are made from milled lithium disilicate (the whiter molars)



Polysilicates involving infinite chains of condensed tetrahedra are quite common. A portion of such a polymeric anionic silicate is shown at right. In order to determine the empirical formula for this polysilicate, we first isolate a "repeating unit" and then use the same bookkeeping as before. One repeating unit has been identified with red the dashed lines in the figure. As a possible strategy, avoid cutting through atoms while identifying a repeating unit – see the green dashed lines. The box isolates three oxygen atoms (remember that the center is a Si and an O) and one silicon atom. Each empirical formula unit carries a -2 charge as described above. What is the empirical formula for the silicate anion shown at above?



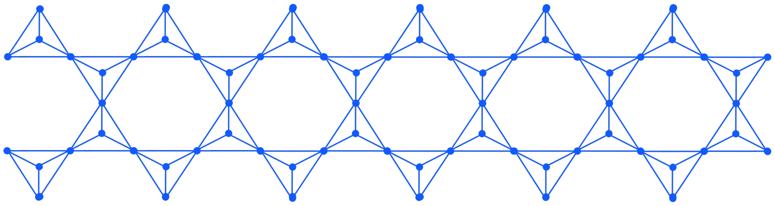
Another common silicate anion is the six-silicon, $Si_6O_{18}^{-12}$, shown at below, along with an example, the gemstone beryl. Green forms of beryl are called emerald.



Beryl, $(Be_3Al_2(Si_6O_{18}))$

Polysilicates such as these are called chain structure polysilicates. They combined with Ca^{+2}, Mg^{+2}, Fe^{+2} and other cations found in nature. When the cations are Ca^{+2}, Mg^{+2}, Fe^{+2} the material is called pyroxenes, a common constituent of basalt. What is the empirical formula of a silicate with two Ca^{+2} for every one of each Mg^{+2} and Fe^{+2}?

Basalt forming hexangonal shaped columns along the shore of Lake Superior at Grand Marais

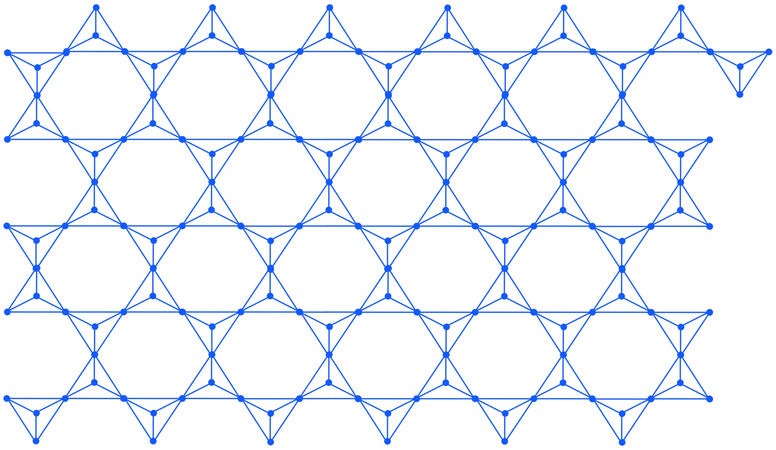


Chain silicates can further condense to form double chain structures such as that shown at right. Keep in mind that only a small segment of a linear polymeric chain is shown here — and the cations are not shown. This complicated structure is the result of condensing a pyroxene anion chain with its mirror image. What is the empirical formula (Hint: $Si_4O_?^{-?}$) and charge for this silicate?

The double chain polysilicate shown above is called an amphibole. These can form fibrous materials providing that the polymeric chains crystallize in a parallel fashion. A familiar example of a fibrous amphibole is asbestos in which case the cations are magnesium and calcium.

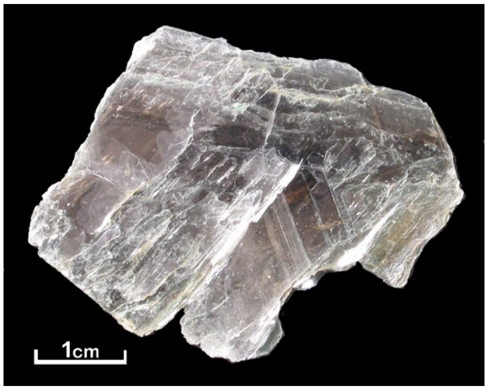
Asbestos (left) and pyroxene (right) both feature double chain silicate anions.

Polysilicates can also form 2 dimensional sheets of condensed tetrahedra. A portion of such a sheet is shown here:



What is its empirical formula for this silicate anion?

As you might imagine, there is considerable bond strength in the 2-dimensional sheet of silicate tetrahedral, typical of network covalent materials. Cations hold these sheets together. In some cases, the cations are all located between alternate sheets — they do not occur between every sheet; alternate sheets are held together only by dispersion forces. For this reason, sheets are easily cleaved from one another. The extremely soft mineral talc (talcum powder) is an example of this sheet-type polysilicate. Talc has the empirical formula $Mg_3(OH)_2Si_4O_{10}$. Micas also utilize the sheet polysilicate structure, however in the case of micas, the cations exist between all sheets. There is a wide variety of minerals that belong to the mica



group. The list of mica cations include H^+, K^+, Al^{+3}, Li^+, Mg^{+2}, and Fe^{+2}.

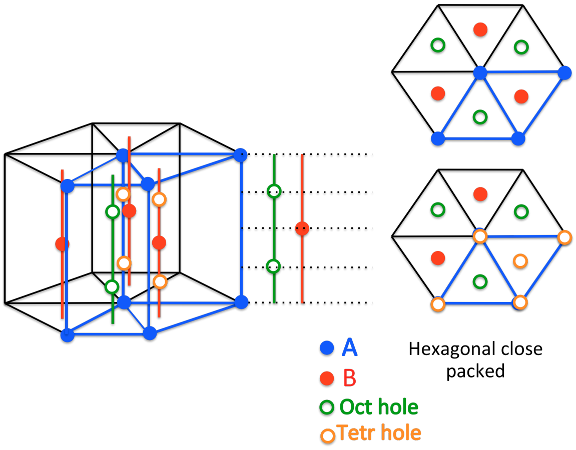
Mica ($^+$, K^+, Al^{+3}, Li^+, Mg^{+2}, and Fe^{+2})($Si_4O_{10}^{-4}$)

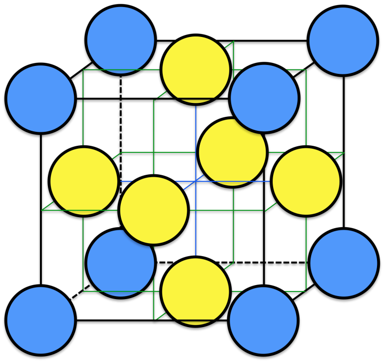
There is one final degree of polysilicate condensation that is possible. This joins the 2-dimensional sheets into a three dimensional structure with formula SiO_2. The mineral quartz has this structure. In quartz, the silicon atoms have a tetrahedral geometry as usual. Each oxygen joins two silicon atoms.

Like all examples of network covalent molecules, SiO_2 has an extremely high melting point. The various forms of SiO_2 have different melting points, however all are in the range of 1600 - 1700 ^oC. The melting point of quartz, one of the more common forms of SiO_2 is 1610 ^oC. SiO_2 in all forms is insoluble in water.

Answers to Day 13:

1. (a) Each fcc unit cell contains 4 spheres, 4 octahedral holes and 8 tetrahedral holes; (b) The ratio of spheres : octahedral holes : tetrahedral holes is for the hcp structure should be the same as for fcc; (c) octahedral holes and tetrahedral holes (left diagram)





(c) Above right: Sketch of one unit cell featuring the chlorides only (colors only denote differences in fcc positions (corner vs face-centers); (c) $e = 4r/2^{0.5}$; (d) the diameter of the octahedral hole is $dia_{oct\ hole} = (2 \times 2^{0.5} - 2)r$, so the radius of the octahedral hole is $r_{oct\ hole} = (2^{0.5} - 1)r$; (e) $(2^{0.5} - 1)r/r = 0.414$

(f) the zinc ions occupy tetrahedral holes in zinc blende. The radius of zinc(II) is 74 pm and sulfide is 170 pm, giving a radius ratio = 0.43; (g) if the small ions are a bit too big, they help to separate the large ions from each other; (h) Li^+, Be^{+2}, B^{+3}, etc.; (i) the radius of a tetrahedral hole is 0.225 r; (l) CsCl; (m) The radius ratio for NaCl is 116 pm/167 pm = 0.695; (n) The coordination number for the filled in ion in the drawing is 12; (o) The coordination number for tetrahedral holes is 4 and for octahedral holes is 6, and for cubic holes is 8.

2. Occupying the octahedral and tetrahedral holes.

(a) half; (b) Perovskite is $CaTiO_3$; (c) NbO; (d) ReO_3; (e) 3/8; (f) (i) all of the octahedral holes are occupied (ii) $e = 2r_{cation} + 2r_{anion}$.

3. Lattice energy and the Born-Haber cycle. (a) $\Delta H_{lattice\ energy} = -2962$ kJ

Step 1. $Mg(s) \longrightarrow Mg(g)$ $\Delta H_{at} = +147$ kJ

Step 2. $Mg(g) \longrightarrow Mg^+(g) + e^-$ $\Delta H_{ion} = +738$ kJ

Step 3. $Mg^+(g) \longrightarrow Mg^{+2}(g) + e^-$ $\Delta H_{ion} = +1451$ kJ

Step 4. $F_2(g) \longrightarrow F(g)$ $\Delta H_{dissociation} = +158$ kJ

Step 5. $2\ F(g) + 2\ e^- \longrightarrow 2\ F^-(g)$ $\Delta H_{elec\ aff} = -656$ kJ

Step 6. $Mg^{+2}(g) + 2\ F^-(g) \longrightarrow MgF_2(s)$ $\Delta H_{lattice\ energy} = ?$

Step 7. $Mg(s) + F_2(g) \longrightarrow MgF_2(s)$ $\Delta H_f = -1124$ kJ

(b) $\Delta H_{lattice\ energy} = -787$ kJ

4. Lattice energies in general. (b) Lattice energies are smallest for +1 and -1 salts. They tend to fall in the range 700 – 1000 kJ. Salts of +2 cations with -2 anions fall in the range 2000 – 4000 kJ/mol. 1:2 and 2:1 salts are intermediate; (c) solubility is greatest for salts with small lattice energies; (d) Phosphates are generally insoluble except for those of Group 1 and ammonium cations; (e) Generally, +1/-1 salts are (soluble), and +2/-2 salts are (insoluble). Sulfates are an exceptions to the generalization, as is AgCl; Among just the +1 and -1 salts, the lattice energy of LiF is the largest due to hard acid-hard base considerations.