

BUILDING CRYSTAL STRUCTURE BALL MODELS USING PRE-DRILLED TEMPLATES: SHEET STRUCTURES, TRIDYMITE, AND CRISTOBALITE

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Overview¹

Ball models have long been used as teaching tools in Mineralogy to illustrate molecular and crystal structures. At Union College, Mineralogy students construct crystal structure ball models to help them better understand the concepts of crystalline order, relative atomic size, atomic coordination, crystal chemistry, and crystal symmetry. We have used two methods for this:

- 1) The students each choose a mineral (an ionic compound) to work on during the second half of the term. They research the mineral origin, occurrence, chemistry, properties, and structure, and write a report. Part of the report is a model of one or more unit cells of the mineral, built using glued together 1/8" to 1" diameter metal and plastic balls (everything from ball bearings to marbles to tennis balls can be successfully used, provided they can be firmly stuck together). The students must choose ball sizes so that they properly fit into the various sites using the radius ratio concept for ionic coordination polyhedra. This type of project has been reasonably successful, but the ball models do not always work out well.

The first problem is that many structures are too difficult for most undergraduates (or me) to build. Garnet and quartz, for example, are two that may look easy, but turn out to be very difficult to build. A related problem is that most silicate and oxide structures are not simple arrays of atoms, like the intersections of lines on graph paper. Small differences between ball radii and the effective (scaled) ionic radii of the real atoms, or small displacements of the balls from atomic positions in the real structures, often result in grossly distorted models. For example, the isometric spinel minerals can be thought of as being based on a cubic closest packed array of oxygens, with the oxygen layers perpendicular to a unit cell body diagonal. In principal, all one should have to do is make the oxygen layers, adding cations in the appropriate places as you go. However, all of the spinel models that have come from these student projects are trigonal.

Several different methods have been used to glue the spheres in the proper places: rulers, clay supports, tape supports, graph paper grids, custom ruled grids, computer drawings, constructing simple subunits of the structures and then combining them, and others. In most cases these methods do not work well since they are not accurate enough or cannot be applied accurately enough. I thought that using pre-drilled templates would allow the straight-forward construction of a limited set of structures, but structures that at least could be successfully built. Since the object is to learn about crystal structures, rather than about model construction techniques, I thought the tradeoff was reasonable.

¹ Sources of the materials we use are given in the Appendix.

- 2) I had two kinds of templates machined: a packed hexagonal array (Figure 1) used for making octahedral layers with $\frac{3}{4}$ " spheres as oxygens or hydroxyls, and an extended hexagonal array (Figure 2) for making corner-sharing tetrahedral layers with $\frac{3}{4}$ " spheres as oxygens. In one 3-hour lab session students use the templates to build various sheet silicate components. The models are then used with sheet mineral hand samples and other props to show the origin of strong pleochroism, the systematics of stacking polytypes, and the reasons for differences in hardness. The models are useful for teaching principles of X-ray diffraction, because the sheets can be stacked and measured to show why the basal spacings of the sheet structures differ. The sheet components that the students make are brucite, serpentine, and talc. These can make brucite, serpentine, talc, biotite (requires some loose K atoms), chlorite, and various clays. Offsets of the paired hydroxyls in the octahedral layers of talc or biotite make it easy to show sheet stacking vectors and the ordering of stacking polytypes. Stacking polytypes can also be demonstrated with oriented layers of Plexiglas[®] hexagons (Figure 3).

The models are fully extended hexagonal sheets, not the less extended trigonal sheets that are so common in nature. Trigonal templates are much harder to design and machine. All of the octahedral layers we make are trioctahedral, since the octahedral vacancies of dioctahedral sheets make the final models too fragile for routine classroom use.

Using templates to make sheet silicate models is easy, accurate, fast, and reliable. Three years of Mineralogy students, working in groups of two, have successfully built their one or two model components in one lab session, with time to spare for discussion of crystal structure, stacking, and using mineral specimens as examples of how properties change with structure (note that each group needs its own templates, so make plenty). The only serious problem has been with excess glue dripping down and cementing the model to the template. This problem can be solved by making the templates of plastic that is resistant to Duco[®] cement, such as polyethylene or polypropylene, instead of Plexiglas[®]. Wood has been tried as a template material, but it is too difficult to make sharp, clean edges on the holes, and so ball locations are not accurate enough. Hot-melt glue guns, for gluing the balls together, have been found by others to work well. Glue guns do not have potentially toxic solvents and the glue cures in seconds, but minor burns are possible. Some glue guns are quite inexpensive.

As the years go by, sheet silicate models accumulate. The individual sheet components are not very useful or instructive, so I do not give them away to the students who made them (although giving away colorful models to students may be good advertising for geology programs). Instead, I keep some model sets for use outside of Mineralogy. Scout troops, for example, love them during mineral demonstrations. I gave away one set (two of each kind of sheet) to a high school earth science teacher, and that is probably what I will continue to do.

What else can the templates be used for? In principal they can be used for any structure that can be approximated by hexagonal arrays of oxygens and/or by fully extended hexagonal tetrahedral layers. Two examples that I include below are tridymite and cristobalite, which are easily made using only the tetrahedral layer template. Reasonably accurate ilmenite and hematite models can easily be made using the octahedral template, although the distorted octahedra will not be distorted in quite the right way. Olivine, spinel, and most other structures based on closest packed arrays of oxygens usually cannot be properly made with these templates. This is because the template octahedra are extended in a plane parallel to the layer to fit the fully extended hexagonal tetrahedral layers in sheet silicates. As a result, the octahedra are strongly

flattened perpendicular to the layers. If you want to make olivine and spinel, drill an octahedral template like that shown in Figure 1, but make the line spacings 0.380" instead of 0.433" for $\frac{3}{4}$ " balls. You will also have to use six-coordinated spheres that have diameters of $\frac{5}{16}$ " rather than the $\frac{7}{16}$ " spheres used here for the sheet silicates.

Crystal and Structural Chemistry of Common Sheet Silicates

All of the common sheet silicates and related minerals are based on two principal components: tetrahedral layers and octahedral layers.

Tetrahedral layers

The tetrahedral layers are nominally hexagonal arrays of corner-sharing SiO_4 tetrahedra. In most natural sheet silicates, small rotations of the Si-O-Si bonds result in arrays that have trigonal symmetry. The shared oxygens in the layer are called "bridging oxygens", since they are the bridges that link adjacent SiO_4 tetrahedra. The other oxygens are called "apex oxygens", since they occupy the 'free' apex of each tetrahedron. Apex oxygens are all shared with cations in the octahedral layer. In talc and some other sheet silicates, Si^{4+} occupies all of the tetrahedral sites. In other sheet silicates Al^{3+} replaces usually $\frac{1}{4}$ but up to $\frac{1}{2}$ of the Si^{4+} ions.

Octahedral layers

The octahedral layers are composed of edge-sharing octahedra, and the layers come in two varieties. In trioctahedral layers all octahedra are occupied, usually by divalent cations such as Mg^{2+} . In dioctahedral layers only $\frac{2}{3}$ of the octahedra are occupied, usually by Al^{3+} .

Connected octahedral and tetrahedral layers

Octahedral layers can be bare, can be attached to a tetrahedral layer on one side, or can be sandwiched between two tetrahedral layers. Bare octahedral layers are obviously not silicates, but since they are layer structures related to and in some cases combined with other layer types, they are included here. In bare octahedral layers, such as brucite, all of the anions are hydroxyls rather than oxygens to maintain charge balance. Each 6-coordinated cation is bonded to 6 hydroxyls. We will ignore the hydrogens of the hydroxyls in our models. The stacking sequence for pure octahedral layer minerals is $\text{O} \sim \text{O} \sim \text{O} \sim \text{O}$, where O represents octahedral sheets stacked up parallel to $\underline{c}$, and ' $\sim$ ' represents weak hydrogen bonds between the sheets.

If the octahedral layer is connected to one tetrahedral layer, as in the 2-layer sheet silicate serpentine, then $\frac{2}{3}$ of the hydroxyls on *one* side of the octahedral layer are replaced by oxygens. These are the apex oxygens of the tetrahedral layer that are shared between the tetrahedral and octahedral layers. Each 6-coordinated cation is bonded to 2 oxygens and 4 hydroxyls. The stacking sequence for 2-layer silicates is $\text{T-O} \sim \text{T-O} \sim \text{T-O} \sim \text{T-O}$, in which T represents tetrahedral layers, O represents octahedral layers, '-' represents strong bonds within the sheets, and ' $\sim$ ' represents weak hydrogen bonds between the sheets.

If the octahedral layer is sandwiched between two tetrahedral layers, as in the 3-layer sheet silicates talc, then $\frac{2}{3}$ of the hydroxyls (as in brucite) on *both* sides of the octahedral layer are replaced by tetrahedral layer apex oxygens. Each octahedral cation is then bonded to two hydroxyls and four oxygens. Again, the oxygens are shared between the octahedral and tetrahedral layers. The stacking sequence for 3-layer sheet silicates is $\text{T-O-T} \sim \text{T-O-T} \sim \text{T-O-T}$, with the symbols as defined above, except that ' $\sim$ ' here represents weak Van der Waals bonds in talc or stronger ionic bonds in micas where K, Na, or Ca occupy the interlayer sites.

Systematic crystal structural chemistry

The table below summarizes the common sheet silicates and related minerals, as distinguished by layer type, layer stacking, and layer composition. The A-site is the 10 to 12 coordinated site nested between the 6-sided rings of facing tetrahedral layers. The A-site may contain K^+ , Na^+ , Ca^{2+} , and other large low-charge ions, and $\square$ (vacancies).

Stack	Layers	A-site	Diocahedral	Triocahedral
$\sim O \sim$	1-layer	None	Gibbsite $\{Al_2U\}(OH)_6$	Brucite $\{Mg_3\}(OH)_6$
$\sim O-T \sim$	2-layer	None	Kaolinite $\{Al_2U\}[Si_2O_5](OH)_4$	Serpentine $\{Mg_3\}[Si_2O_5](OH)_4$
$\sim T-O-T \sim$	3-layer	U	Pyrophyllite $U\{Al_2U\}[Si_4O_{10}](OH)_2$	Talc $U\{Mg_3\}[Si_4O_{10}](OH)_2$
$\sim T-O-T \sim$	3-layer mica	K^+	Muscovite $K\{Al_2U\}[AlSi_3O_{10}](OH)_2$	Biotite (Phlogopite) $K\{Mg_3\}[AlSi_3O_{10}](OH)_2$
$\sim T-O-T \sim O \sim$	4-layer	None	None?	Chlorite $\{Mg_3\}[Si_4O_{10}](OH)_2 \cdot \{Mg_3\}(OH)_6$

T = Tetrahedral layer in the stack.

O = Octahedral layer in the stack.

{ } = Octahedral layer cations in the formulae.

[] = Tetrahedral layers in the formulae.

The coupled substitution $3^{[6]}M^{2+} \Leftrightarrow 2^{[6]}Al^{3+} + ^{[6]}U$ controls the composition difference between diocahedral and triocahedral structures. The coupled substitution $^{[12]}U + ^{[4]}Si^{4+} \Leftrightarrow ^{[12]}K^+ + ^{[4]}Al^{3+}$ controls the composition difference between 3-layer sheet structures having empty (e.g., talc) vs. occupied (e.g., biotite) A-sites. Na^+ and Ca^{2+} are major A-site ions in some micas. A common substitution in micas, chlorite, and some serpentines is the coupled substitution $^{[6]}Mg^{2+} + ^{[4]}Si^{4+} \Leftrightarrow ^{[6]}Al^{3+} + ^{[4]}Al^{3+}$ (the Tschermak substitution), which makes most micas and chlorite more Al-rich than the basic formulae. Many medium-size ions can substitute in the octahedral sites, including Fe^{2+} (almost universal), Ni^{2+} , Co^{2+} , Fe^{3+} , V^{3+} , Cr^{3+} , Li^+ , and Ti^{4+} . Obviously some substitutions are simple and some are coupled, depending on the ion and the sheet silicate into which it is substituting. No ions other than Si^{4+} and Al^{3+} are abundant in tetrahedral sites.

Stacking polytypes

Despite the nominally hexagonal shape of the sheets, sheet silicates do not generally have hexagonal symmetry. First, tetrahedral layers must usually shrink a little to fit the more rigid octahedral layers. Tetrahedral layers do this by slight rotations of Si-O-Si bridging oxygen bonds, becoming trigonal in the process. Second, paired hydroxyls and tetrahedral layers on either side of each octahedral layer in micas and talc are offset from one another (Figure 4). Each sheet, therefore, has an intrinsic polarity known as the stacking vector (Figure 5). The vectors of stacked sheets may all point in the same direction in a crystal, or they may point in different directions in a repeating pattern or randomly up the stack (the c axis; Figure 6). Sheet silicates that are identical but for the stacking vector repeat pattern are polymorphs, but are referred to as polytypes since they are physically almost identical to one another. X-ray

diffraction, however, can spot the characteristic repeat spacing of the stacking vector. There are six simple types of stacking vector repeats, presented in the table below and in Figure 6.

Polytype name	Sheets/ repeat	Crystal system	Stacking vector rotation/layer	Symmetry element ° c
1M	1	Monoclinic	none	mirror.
2M ₁	2	Monoclinic	60°	c̄ glide.
2M ₂	2	Monoclinic	120°	c̄ glide.
2O	2	Orthorhombic	180°	c̄ glide.
3T	3	Trigonal	120°	3 ₁ screw axis
6H	6	Hexagonal	60°	6 ₁ screw axis
M _d	Disordered	Monoclinic	Disordered	mirror

Look in a mineralogy text to see which minerals commonly have which stacking polytypes.

Building the Models: Instructions to Students

Sheet silicates

Sheet silicates are among the easiest silicate models to make. Most sheet silicates do not have perfect hexagonal arrays, but rather are slightly distorted with trigonal symmetry. Even in the rare sheet silicates with perfectly hexagonal arrays (e.g., the Fe-rich biotite annite), the sheets stack to yield monoclinic, trigonal, orthorhombic, or hexagonal crystals. Our models will have completely extended, perfectly hexagonal arrays since it makes no difference to the symmetry of the final crystals, and it makes the models easier to build.

You will work in teams of two building parts for a variety of trioctahedral sheet structures. It is not difficult to build accurate models, since most of the atoms will be located using precisely machined templates. The glue tends to be a bit of a mess. Do your best to keep glue off the templates, and keep paper towels handy to wipe up excess glue. Each team will build parts of various sheet structures, including 3-layer talc sheets, 2-layer serpentine sheets, and 1-layer brucite sheets. Using these components, and unglued K⁺ ions, we will be able to construct a variety of mica, clay, and hydroxide structures. Dioctahedral sheet silicates are easy to build in principle, but in practice the models are too fragile.

Gluing is the hardest part of making ball models. The best way to do it is to put a ball in place first to see where it makes contact with others. Then remove the ball, put small blobs of glue at the contact points, and fit it back together. Make sure the glue is at the contact points, and leave the glue to dry. Don't let the glue drip down onto the template.

Atoms and the balls that represent them are shown in Figure 7. For talc, follow the instructions in Figures 8 to 12. For serpentine, follow the instructions in Figures 8, 13, and 14. For brucite, follow the instructions in Figures 13 and 15.

In the serpentine and talc models one tetrahedral layer is completely removable from the octahedral layer. This allows you to see how oxygens are shared between layers, and to see the 6-coordinated ions that are otherwise hidden. A-site vacancies of talc can be filled with loose K⁺ ions to make biotite.

Tridymite and Cristobalite

Tridymite and cristobalite are polymorphs of silica, SiO_2 . They are two of the nine known thermodynamically stable, condensed silica phases (Figure 16): α and β quartz, α and β tridymite, α and β cristobalite, coesite, stishovite, and liquid. Other low-temperature phases that have limited or no true stability fields are moganite and keatite. A new silica polymorph, structurally similar to baddeleyite (ZrO_2), has been predicted on theoretical grounds to be the stable silica polymorph at deep mantle pressures (Belonoshko, et al., 1996).

In their stability fields tridymite and cristobalite can both undergo displacive phase transformations: tridymite from the low temperature trigonal α form to the high-temperature hexagonal β form, and cristobalite from the low temperature tetragonal α form to the high temperature isometric β form. Tridymite also undergoes several metastable polymorphic transformations at temperatures below those of its stability field (Heaney et al., 1994).

The tridymite structure is based on the stacking of alternating layers of corner-sharing silica tetrahedra. Within each layer up- and down-pointing tetrahedra alternate. The layers are stacked so that up-pointing tetrahedra in one layer share oxygens with the down-pointing tetrahedra in the layer above. The layers are arranged to form hexagonal channels parallel to the c crystallographic axis. If you look down the c axis of the structure (Figure 17A), down-pointing tetrahedra of one layer completely hide the up-pointing tetrahedra in the layer below; all the tetrahedral bases are oriented the same way. The structure of hexagonal β tridymite is related to that of lonsdaleite, the hexagonal polymorph of diamond². Silicon in tridymite occupies the same positions as carbon in lonsdaleite, and the oxygens occupy positions corresponding to the C-C bonds.

The cristobalite structure is related to that of tridymite. It, too, is built up of layers of corner-sharing silica tetrahedra, and in each layer up- and down-pointing tetrahedra alternate. However, in cristobalite the layers have three possible positions rather than two, and the hexagonal channels seen in tridymite are blocked. If viewed perpendicular to the layers (Figure 17B), the tetrahedra in one layer are rotated 60° from tetrahedra to which they are linked in the underlying layer. Unlike tridymite, the overlying tetrahedra do not completely hide underlying tetrahedra. Isometric β tridymite has a structure related to that of diamond: silicons occupy the same positions as carbon in diamond, and oxygens occupy positions corresponding to the C-C bonds.

For tridymite, follow the directions in Figures 18 and 19. For cristobalite, follow the directions in Figures 20 to 23. The high-symmetry β polymorphs are made here since templates for them are much easier to design and machine than those for the lower symmetry α polymorphs.

² Lonsdaleite and diamond have structures identical to wurtzite and sphalerite, respectively, if you pretend that all of the atoms in the sulfides are carbon.

General References

- Bailey, S.W., Editor (1984) Micas. Mineralogical Society of America, Reviews in Mineralogy, v. 13.
- Bailey, S.W., Editor (1988) Hydrous Phyllosilicates (Exclusive of Micas). Mineralogical Society of America, Reviews in Mineralogy, v. 19.

References Cited

- Belonoshko, A.B., Dubrovinsky, L.S. and Dubrovinsky, N.A. (1996) A new high-pressure silica phase obtained by molecular dynamics. *American Mineralogist*, v. 81, p. 785-788.
- Klein, C. and Hurlbut, C.S. Jr. (1993) *Manual of Mineralogy*, 21st Edition. John Wiley and Sons, Inc., New York.
- Heaney, P.J., Prewitt, C.T. and Gibbs, G.V. (1994) Silica: Physical Behavior, Geochemistry, and Materials Applications. Mineralogical Society of America, Reviews in Mineralogy, v. 29, 606 p.
- Thompson, J.B., Jr. (1981) An introduction to the mineralogy and petrology of the biopyriboles. In Veblen, D.R., Editor, *Amphiboles and Other Hydrous Pyriboles—Mineralogy*, p. 141-188., Mineralogical Society of America, Reviews in Mineralogy, v. 9A.

Appendix: Sources for Materials

Plastic sheeting:	Plastic spheres:
United States Plastic Corp.	Ace Plastics, Inc.
1390 Neubrecht Rd.	26 North Ave.
Lima, Ohio 45801	Garwood, NJ 07027
800-537-9724.	800-695-4223