DIRECTED-DISCOVERY OF CRYSTAL STRUCTURES USING BALL AND STICK MODELS

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INTRODUCTION

Understanding relationships in three dimensional objects, whether crystal structures or the architecture of mountain belts, presents formidable barriers to understanding for many students in the geosciences. Students may have a difficult time mastering concepts of crystallography and crystal chemistry because a) it is typically their first formal encounter with 3-D visualization, b) the crystal structures may appear to be too complex and abstract, and thus overwhelming for many students, and c) instruction on crystal structures may be out of context with respect to other course content or future geologic applications. Two-dimensional representations of crystal structures presented as line drawings or perspective diagrams in textbooks are inadequate to convey fundamental 3-D relations to students. Use of computer models (e.g., SHAPE and ATOMS, see contributions of Brock and Velbel, this volume) and building crystal models (see Hollocher, this volume) provide significant improvements in instruction on crystal structures. Although computer simulations are useful for many crystallographic representations, it is also necessary to provide students with opportunities to work with physical materials. This exercise provides a series of activities in which students manipulate ball and stick models to discover for themselves the underlying relationships of crystal structures and the principles of crystallography and crystal chemistry.

One of the key recommendations of *Project 2061 Science for All Americans* (AAAS, 1989) is "start with the concrete and work towards the abstract". In this regard, ball and stick models are great materials for students to explore as they first encounter the internal arrangement of atoms in minerals. The increased emphasis on "hands-on", and more importantly, "discovery-based" learning experiences is effectively implemented as students manipulate ball and stick models. But open-ended discovery, i.e. turning the students loose without specific instructions or expectations of outcomes, may prove to be very frustrating to students. They may not know where to start, what to look for, or how to interpret the various relationships. I advocate a "directed-discovery" approach in which students are given specific instructions on where to look for relationships, but they must find these relationships for themselves. It is also important that directions be given to a) place the observations in appropriate contexts with respect to fundamental chemical and physical principles, and b) make connections to other bodies of knowledge that have already been covered, or in anticipation of new material that will be covered, in the course.

In this series of exercises, a kind of reductionist approach is used to direct the students attention to specific characteristics of a variety of ball and stick models. Through a series of leading questions, students must focus on specific relationships and must rationalize these relationships according to the fundamental principles of crystal chemistry and crystallography. In this way, students will simulate and replicate the kinds of questions we would normally ask in our professional careers as mineralogists. This approach also addresses other major recommendations from *Project 2061*: start with questions about nature, and concentrate on the collection and use of evidence. Other questions ask students to make connections to basic chemistry (e.g. bond types, relative strength of bonds, bond angles), determinative mineralogy (most likely place to develop cleavage), analytical techniques (e.g. preferred orientations for X-ray analysis), and so on. The final reflection questions will allow students to "discover" Pauling's Rules, a much more effective learning strategy than simple memorization of these rules (commonly with little or no understanding on the part of the students).

The ball and stick models may be used in a number of different instructional modes. It may be necessary for you to provide a demonstration to the class, pointing out the relationships that can be seen in a given model, showing how to look at the crystal in different orientations, identifying the location of close packed layers of oxygen, pointing out similarities among sites with balls of the same color, noting the presence of voids in the structures, etc. It may be appropriate to put the models out for self-paced learning exercises, allowing the students to spend as much time as they need on a given model before they move on to the next. I have found that interactive learning strategies (see Srogi and Baloche, this volume) are particularly effective. Try the jigsaw technique by assigning small groups of students to be the "experts" on a given crystal structure, and then reassign students to new groups to teach each other about the important relationships for each assigned structure. Have the "experts" compare similarities among different structures such as different types of tectosilicates, or between pyroxenes, amphiboles, and micas. Outcomes could be written short answers to the questions, longer integrative writing assignments, or verbal articulation of answers to peers or instructors. If you have a collection of ball and stick models, refer to these throughout the course to make connections between different content areas in reference to determinative properties of minerals, to introduce new mineral groups in hand sample, to introduce the techniques of X-ray diffraction, and to explain why different minerals give different powder (or precession) patterns, etc.

The ball and stick models described below are common structures or rock-forming minerals that I happen to have in my collection. These models are expensive, and you may have access to only a few. You may find that some of these models are stashed away in other departments (chemistry, physics, materials sciences; it's worth looking around). In any case, in-depth exploration of any 3-D crystal models through directed discovery will be a beneficial learning experience for students. Amend these questions to meet your own instructional needs, or use these questions as models for developing similar exercises for other crystal models.

ASSIGNMENT

For each of the crystal models, identify the features outlined in the following questions. A starting orientation is suggested for each model, but you should also physically rotate all the models to look at them from many directions. Pay special attention to the different types of atoms represented in each structure (different colored balls). Note what other atoms are "in the neighborhood" and how many nearest neighbor atoms are in the structure. Check to see if each cation is in an electronically neutral environment (or nearly so). Note the bond lengths and bond angles. For minerals with oxygen as the dominant anion look for close packed arrays of oxygen. Look for coordination polyhedra and ways in which these polyhedra come together to form the overall structure. Look for regular repetitions of atoms or groups of atoms (i.e. symmetry). All references to figures and pages numbers are to Klein and Hurlbut (1993) *Manual of Mineralogy*, John Wiley & Sons. Use this text as a reference to help with your understanding of the crystal structures. For more detailed descriptions of crystal structures, consult the Reviews in Mineralogy series, published by the Mineralogical Society of America. The models used are from Klinger Educational Products.

Magnesium metal (see Fig. 10.1, p. 337)

a) All of the atoms have the same atomic radius. What is the coordination number of any Mg atom in this structure?
b) Stand the model on the three metal legs. What is the stacking arrangement of the layers (ABCABC, or ABAB)? Is this a CCP or HCP structure?
c) Look directly down on the model in the above orientation. Rotate the model 120°. Do similar atoms occupy exactly the same positions, or are they in a different arrangement? Try the same with a 90° and 180° rotation.

Graphite, C, (see Fig. 10.8, p. 344)

a) What is the coordination number for each C atom in the horizontal planes?
b) What kind of orbitals does C have in this structure?
c) What type of bonds occur within the layers, and between the layers?
d) What is the bond angle between C atoms in the horizontal planes?
e) Describe the geometrical arrangements of C atoms that repeat in similar patterns in the horizontal planes. How many atoms occur in these groups?
f) Look directly down on the horizontal plane. Rotate the structure until similar atoms occupy identical positions. How many degrees of rotation are needed to repeat this structure? Note the relationship between bond angle and atomic positions.
g) Look at the model from a side view. Now flip it over, top to bottom (180°). Do the atomic positions exactly repeat themselves?
h) Describe any planes (horizontal or vertical) that might pass through the crystal such that atomic positions on one side of the plane are exactly the same as atomic positions on the other side.
I) How many cleavages would you expect in graphite? What is the hardness of graphite? What controls this physical property?

Diamond, C, (see Fig.10.8, p. 344)

a) What is the coordination number for each C atom?
b) What is the shape of the polyhedron that forms if all of the nearest neighbor C atoms are connected?
c) What type of orbitals does a C atom have in this type of structure?
d) What type of bonds occur in diamond? What are the bond angles?
e) What is the relationship between bond type and hardness? Bond angle and cleavage? How many cleavage planes would you expect in diamond. Try to locate these on the structure.
f) Stand the model on its legs and look directly down. Inside the structure there is the outline of the cubic unit cell, outlined by heavier metal rods. Look down the long, body diagonal of the cube. Rotate 120° and see if the atoms occupy the same exact positions. Try this for the other long body diagonals of the unit cell cube.
g) If you find a flat, square face of the unit cell cube, you might expect that a 90° rotation will repeat the atomic arrangement. It does not! Explain why. (Hint: look up the meaning of 4-fold screw axis.)
h) How can C occur in two different types of crystal structures? (Hint: look up the meaning of polymorph.)

Wurtzite, ZnS, Zn=silver, S=yellow (see Fig. 10.23, p. 357)

a) What is the coordination number for Zn? For S?
b) The Zn and S atoms are each in a close packed structure. What kind?
c) What type of bond forms between the S and the Zn?
d) Look down onto the central S atom. What is the symmetry (e.g. How many degree rotation is necessary to replicate the same atomic positions)?

Halite, NaCl , Na=silver, Cl=red (see Fig. 4.42, p. 211; Fig. 11.37, p. 398)

a) What is the coordination number for Na?
b) What type of polyhedron forms around the cations?
c) What type of bond occurs in NaCl? Is it a directional bond?
d) How many cleavages occur in NaCl? What is the angle between them?
e) Look at a single row of atoms that are perpendicular to one of the flat faces. What is the symmetry in this direction?
f) Look at the body diagonal (i.e. stand the model on one of the corners). Look down this diagonal and determine the symmetry. How many identical rotation axes occur in this structure?
g) Identify any planes in the structure that exactly replicate positions of the same kinds of atoms equidistant on both sides of the plane. How many sets of planes occur in this structure (these will have the same orientation); what is the angular relation between different sets of planes?

Cesium Chloride, CsCl, Cs=silver, Cl=red (see Fig. 4.43, p. 211)

a) What is the coordination number of Cs?
b) What is the polyhedron that forms around Cs?
c) Compare the structures of NaCl and CsCl. Why are they different? (Hint: use the periodic table.)
d) Which is more soluble, NaCl or CsCl, and why? Which element, Na or Cs, will most readily fit into mineral structures, which will be excluded during a crystallization sequence (i.e. it will be concentrated in a magma) and why?

Calcite, $CaCO_3$, Ca=silver, C=black, O=red (see Fig. 12.2, page 404)

a) What is the coordination number of C ? (see Fig. 4.22 G, p. 194)
b) What is the radius ratio (cation/anion) for carbonates?
c) Note that the calcite structure contains alternating planes of carbonate complexes and Ca atoms.
d) Look down the axis of the rhomb (body diagonal). What is the symmetry? Is this consistent with the bond angles in the carbonate complexes?

Spinel, $MgAl_2O_4$, Mg=wood, Al=silver, O=red (see Fig. 11.5, p. 375; Fig. 11.6, p. 376; Fig. 4.48, p. 213-214)

a) Stand the model on the long diagonal, with a silver ball on top. Note the horizontal planes of close packed oxygen. Is this HCP or CCP?
b) What is the coordination number for Mg? For Al?
c) Note the numerous "voids" in the structure. Why are they present? What percentage of the possible tetrahedral sites, and what percentage of the possible octahedral sites are filled?

d) Note the overall cubic form of this structure. Look down any of the long, body diagonals of the structure and you will see that these are 3-fold axes. How many 3-fold axes are present? There are more symmetry elements present in this structure but they are difficult to find because they are complicated combinations of glide planes and screw axes.

Olivine,$(Mg,Fe)_2SiO_4$, O= red, Mg,Fe=silver, Si=black; (see Fig. 13.4, p. 445)

a) What is the coordination number of Si, and Mg?
b) What is the relationship of the Si tetrahedra? Are they somehow connected to each other or are they independent of each other? Hint: look at the corners of the Si polyhedra and see what they are connected to in the structure.
c) What is the relationship of the Si and Mg polyhedra? Are they connected to each other? If so, how are the Si and Mg polyhedra connected (what structural components do they share)?
d) Orient the model so that the shortest dimension is vertical, and the longest axis is left and right. From the side, note the layers of O atoms. From the top, note the close packed array of O. Can you predict the position of the next series of O atoms as this structure is extended into space (i.e. during crystal growth)? Rotate the crystal on the table (i.e. look from the side) until rows of Mg atoms are perfectly aligned. This same procedure of rotating crystals into preferred orientations is essentially what is done during single crystal X-ray analysis to determine crystallographic parameters such as measurement of unit cell dimensions and interaxial angles.
e) Compare the olivine structure to the spinel structure. Both have model formulas of XY_2O_4 (i.e. one tetrahedral site and two octahedral sites). Which mineral appears to have greater symmetry? Which mineral appears to have a greater density? Olivine and spinel minerals are both found in the mantle. Which structure will be favored by very high pressures, and why?

Diopside $CaMgSi_2O_6$; O=red, Si=black, Mg=silver, Ca=gold; see Fig. 13.48 p. 477

a) Orient the model so that the shortest dimension is front to back and layers of oxygen roughly alternate with layers of Ca and Mg. What is the coordination of Si, Mg, and Ca?
b) Focus on the Si tetrahedra and their arrangement in this structure. Diopside is an "inosilicate" or "single chain silicate". Look carefully and find the chain of Si tetrahedra. Within a given chain, how are the Si tetrahedra connected to each other? The oxygen atom that connects adjacent tetrahedra along the chair are called bridging oxygens. Look at a chain internal to the crystal, and note that 3 of the oxygen in each polyhedron are roughly in the same plane, and that a fourth oxygen in each tetrahedron "points" either up or down. What is this oxygen connected to? Are any of the chains of Si tetrahedra directly connected to any other chain?
c) Compare this 3-D view of diopside with the perspective drawing in figure 13.49 (p. 477). This view is looking down the c-crystallographic axis. Note that when viewed down the length of the chain, alternating Si tetrahedra are slightly offset. Each chain of tetrahedra will be connected to an adjacent octahedral layer by the fourth oxygen (noted above), and this octahedral strip will also be connected to a second tetrahedral chain on its other side. This produces the T-O-T structure of alternating tetrahedral-octahedral-tetrahedral layers, commonly referred to as the "I-beam" structure. Make sure that you can identify this basic structure in the ball and stick model.
d) Compare the directions of the cleavage planes illustrated in figure 13.49 and see if you can find their location on the model structure. What are the relative bond strengths within the Si tetrahedra compared with bonds involving octahedral sites?
e) Turn the model 90° (looking at the smallest face). This view shows the c-axis (left and right) and the a-axis (near vertical). Note that the structure appears to be "inclined" or tilted to one side. Imagine a line that connects identical atoms on the top plane and bottom plane (e.g.

identical Ca or Mg atoms) this is the a-axis, and a line parallel to the chains of Si tetrahedra is the c-axis. The angle between these two lines is the β angle (the angle between a and c axes) which is > 90° for monoclinic crystals such as diopside.

Tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$ O=red, Si=black, Mg=silver, Ca=gold, OH=green (see Fig. 13.66 and 13.67, p. 490)

a) Orient the model such that the longest dimension is left-right, and the shortest dimension is front-back. What are the coordination numbers of Si, Mg, and Ca?

b) Focus on the narrow, central part of the model. Tremolite is a "double-chain" silicate. Locate the two linked chains of Si tetrahedra. (Hint: these will occur front to back with the model in this orientation; this is parallel to the c-crystallographic axis.) Describe how the tetrahedra are linked to form each chain. Find the "bridging oxygen" which connects the two chains. If the model were extended in space, predict the location of the next bridging oxygen for additional unit cells in front and behind.

c) Continue to focus on the center of the model. Note that the top double chain has the tetrahedra with an apex pointing "down", and the bottom double chain has the free apex pointing "up". What type of crystallographic sites are located in between these double chains? This structure of alternating tetrahedra-octahedra-tetrahedra sites, or T-O-T, forms the basic architecture of the amphibole group. Look at the model from the front side and compare with figure 13.67. The T-O-T structure is also referred to as "I-beams" because of their shape in cross section. Note the relationship of adjacent I-beams how are they connected in the structure?

d) Locate the silver balls in the center of the structure. The two silver balls in the front and back of the structure are identified as the M1 sites (M refers to metal, Mg in this case). The three balls in the center are referred to as the M2 sites (on both ends) and M3 (in the center). Note that the gold balls (Ca) have a higher coordination number, and therefore, occupy unique crystallographic sites, known as M4. What is the relative ionic radius of Ca compared to Mg?

e) Figure 13.66 is a perspective view of the tremolite structure seen from the "top" of the model (the long dimension is the crystallographic b-axis, and the front-back direction is the crystallographic c-axis). Compare the atomic positions in the model to this perspective drawing.

f) Note that some of the expected positions of oxygen (red balls) are occupied by hydroxyl complexes (green balls). Why does this occur?

g) Note that there are some very large sites in the structure. These are known as the A-sites. What is the coordination of these sites? These sites are empty for tremolite, but are commonly filled, or partially filled , for other amphiboles. What elements would be expected to occur in these sites? If the A-site is partially filled, what also must happen elsewhere in the structure? (Hint: look up the mechanism for coupled solid solutions.)

h) Compare the tremolite (amphibole) structure to the diopside (pyroxene) structure. What aspects of these crystal structures are similar, and how are they different? Look at figure 13.69, 13.70, 13.71 (p. 492-493). A class of related minerals is called "biopyriboles". Note that it is possible to have not only single and double chains, but also triple chains, and these structures can alternate within a single crystal.

I) Describe the most likely position of cleavages in this structure (see Fig. 13.67).

Biotite $K(Mg,Fe)_3(AlSi_3)O_{10}(OH)_2$; O=red, Si=black, Mg,Fe=silver, K=gold, OH=green (see Figs. 13.82, 13.83 these are related structures of pyrophyllite and muscovite; p. 500; 13.84, p.502)

a) What are the coordination numbers for Si, Mg, K?
b) How are the Si tetrahedra connected in this structure (i.e. how many corners are connected to other tetrahedra, in what direction are the unconnected apices of the tetrahedra pointed)?
c) Note that the basic structure consists of layers of Si tetrahedra on top and bottom of sheets of octahedral (Mg, Fe) sites; this, again is the T-O-T structure.
d) Focus on the atomic sites for K. Are these relatively strong or weak bonds? Where is the most likely place to find cleavage in this mica?
e) Look on the "top" of the model (perpendicular to the sheets). What is the apparent symmetry of the "rings" of Si tetrahedra? Note that the sheets of tetrahedra are not stacked directly over the layer below. What is the symmetry of biotite if the stacked layers are "inclined" with respect to each other?
f) Compare the biotite structure to the structures of amphiboles and pyroxenes. How are they similar, how are they different?

Alpha Quartz, SiO_2, Si=black, O=red;

a) What is the coordination number of Si?
b) What types of bonds are present?
c) What is the hardness of quartz? What is the melting point? How are these physical properties related to bond type and strength?
d) Compare the structure of diamond and quartz. Are there similarities?
e) Describe how the Si tetrahedra are joined in this structure.

Sanidine, $KAlSi_3O_8$; O=red, Si,Al=black, K=gold; fig 13.118, p. 533; Fig. 13.119, p. 534

a) Orient the structure so that two gold balls are near the bottom, and the model is standing on two sets of 5 oxygen balls. What are the coordination numbers of Si,Al (black balls) and of K?
b) How are the tetrahedral sites connected in this structure?
c) Look at the side of the model. Focus on the vertical plane that contains the gold balls in the center. How do the crystallographic sites compare on the left and right side of this model? The long dimension of this model is parallel to the crystallographic b-axis. Compare this view with Fig. 13.118.
d) Look down the b-axis. Rotate the model around this axis. Do the atomic positions exactly repeat themselves after 90° , 120° or 180° rotation? (Hint: look down the center of the "channels" as seen in this orientation.)
e) All of the tetrahedral sites are essentially the same in this model. What would happen to the symmetry if the structure was "ordered" such that every fourth tetrahedron was somehow unique (e.g. in its size or shape). Try labeling tetrahedral sites in this manner with a small piece of tape and see if the symmetry increases or decreases.
f) You now know where the b-axis is in this structure. Use figure 13.119 to help you locate the "crankshaft" structure in this model. (Hint: a=8.56 Å, b=13.03Å, c=7.17Å; K&H p. 541; you need to find the unit cell orientation that contains the two largest crystallographic dimensions to get the same perspective as the drawing in this figure.) You will see only a couple of repeat units along the a-axis.

Summary Questions

1. What are the two basic ways that close-packed planes of oxygen can be stacked to form three dimensional crystal structures?
2. In all of the crystal structures you have observed, the various cations have filled voids in layers of anions. Construct a chart that includes the following: number of "nearest neighbor" anions, type of coordination polyhedra, the radius ratio for cations and anions (Rc/Ra) (see Bloss 1971 p. 230-235 or K&H, p. 190-197), and for silicate minerals (with O as the principal anion) the elements that would be expected to go into each site. Look at the periodic table and see if there is a pattern regarding which groups of elements are most likely to occur in different crystallographic sites.
3. For different types of coordination polyhedra in the various models, what is the charge of the cation in the polyhedron, and how much charge is "shared" from each of the nearest neighbor anions? Is the charge on the anion balanced by shared charge from the surrounding cations? Has the overall structure achieved electrostatic neutrality? Is this generally true for the structures that you have studied?
4. Look carefully at the ways in which coordination polyhedra come together to form a 3-D crystal structure (the silicate models are best to review; compare with the perspective drawings in your text book). Do the polyhedra tend to share single points, edges, or faces? Explain this relationship.
5. Focus on polyhedra that have small coordination numbers and contain elements with high valence. Do these polyhedra tend to be concentrated within the crystal structures, or do they tend to be dispersed?
6. You have looked at a number of different types of crystal structures that are representative of a large part of the mineral kingdom. In general, is there a large variety of crystallographic sites in any of the crystal structures, or do the types of crystallographic sites tend to be small?
7. Compare your answers to the above questions with the discussions on "Pauling's Rules" from Bloss (1971, p. 235-245 or K&H p. 197-201). Congratulations! You have just rediscovered the fundamental principles of crystal structures that were first described by Linus Pauling in 1929, and which led to his award of the Nobel Prize for Chemistry in 1954.

Source of Crystal Structure Models

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