Crystallography

- **Motif**: the fundamental part of a symmetric design that, when repeated, creates the whole pattern
- In 3-D, **translation** defines operations which ‘move’ the motif into infinitely repeating patterns
- M.C. Escher’s works are based on these ideas
Symmetry → Crystallography

• Preceding discussion related to the shape of a crystal
• Now we will consider the internal order of a mineral…
• How are these different?
Growth of crystal is affected by the conditions and matrix from which they grow. That one face grows quicker than another is generally determined by differences in atomic density along a crystal face.
Crystallography

- **Motif**: the fundamental part of a symmetric design that, when repeated, creates the whole pattern
- In 3-D, *translation* defines operations which ‘move’ the motif into infinitely repeating patterns
- M.C. Escher’s works are based on these ideas
Translations

This HAS symmetry, but was GENERATED by translation…
Translations

2-D translations = a net

Unit Cell: the basic repeat unit that, by translation only, generates the entire pattern – can you pick more than 1 unit cell?

How differ from motif ??
Translations

Which unit cell is correct??

Conventions:

1. Cell edges should, whenever possible, coincide with symmetry axes or reflection planes.
2. If possible, edges should relate to each other by lattice’s symmetry.
3. The smallest possible cell (the reduced cell) which fulfills 1 and 2 should be chosen.
Unit Cell

• How to choose a unit cell if more than one unit cell is a possibility…
• Rule: Must represent the symmetry elements of the whole!
3-D translations

- Operations which ‘move’ a motif create the **lattice** – a representation of the ‘moves’ which create the pattern in plane or 3-D space

- **Unit cell** is a representation of the crystal such that it can be repeated (by moving it) to make that pattern
  - If a crystal has symmetry, the unit cell must have at least that much symmetry
Unit cells have at least as much symmetry as the crystal (internal order > external order)

- Here is why there are no 5-fold rotation axes! If the unit cell cannot be repeated that way to make a lattice, then a crystal cannot have that symmetry…
(a) cubic  (b) tetragonal  (c) orthorhombic
(d) hexagonal  (e) monoclinic  (f) triclinic

<table>
<thead>
<tr>
<th>Unit Cell Shape</th>
<th>Crystal System</th>
<th>Unit Cell Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>cubic</td>
<td>cubic (isometric)</td>
<td>4/m32/m</td>
</tr>
<tr>
<td>tetragonal</td>
<td>tetragonal</td>
<td>4/m2/m2/m</td>
</tr>
<tr>
<td>hexagonal</td>
<td>hexagonal</td>
<td>6/m2/m2/m</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>2/m2/m2/m</td>
</tr>
<tr>
<td>monoclinic</td>
<td>monoclinic</td>
<td>2/m</td>
</tr>
<tr>
<td>triclinic</td>
<td>triclinic</td>
<td>1</td>
</tr>
</tbody>
</table>
3-D Translations and Lattices

- Different ways to combine 3 non-parallel, non-coplanar axes
- Really deals with translations compatible with 32 3-D point groups (or crystal classes)
- 32 Point Groups fall into 6 categories

<table>
<thead>
<tr>
<th>Name</th>
<th>axes</th>
<th>angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha = \gamma = 90^\circ \beta \neq 90^\circ$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a_1 = a_2 \neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a_1 = a_2 = a_3 \neq c$</td>
<td>$\beta = 90^\circ \gamma = 120^\circ$</td>
</tr>
<tr>
<td>Hexagonal (4 axes)</td>
<td>$a_1 = a_2 = a_3$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$a_1 = a_2 = a_3$</td>
<td>$\alpha = \beta = \gamma \neq 90^\circ$</td>
</tr>
<tr>
<td>Isometric</td>
<td>$a_1 = a_2 = a_3$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
</tbody>
</table>

Axial convention: “right-hand rule”
Unit cell types

- Correspond to 6 distinct shapes, named after the 6 crystal systems.
- In each, representations include ones that are:
  - Primitive (P) – distance between layers is equal to the distance between points in a layer
  - Body-centered (I) – extra point in the center
  - End-centered (A,B,C) – extra points on opposite faces, named depending on axial relation
  - Face centered (F) – extra points at each face
- Cannot tell between P, I, A, B, C, F without X-ray diffraction. Can often tell point group, system (or class), and unit cell shape from xstal morphology.
Unit cells – counting motifs (atoms)

- $Z$ represents the number of atoms the unit cell is comprised of

- Atom inside cell counts 1 each
- Atom at face counts $\frac{1}{2}$ each
- Atom at edge counts $\frac{1}{4}$ each
- Atom at corner counts $\frac{1}{8}$ each
Bravais Lattices

• Assembly of the lattice points in 3-D results in 14 possible combinations
• Those 14 combinations may have any of the 6 crystal system (class) symmetries
• These 14 possibilities are the Bravais lattices
Monoclinic
\[ \alpha = \gamma = 90^\circ \neq \beta \]
\[ a \neq b \neq c \]

Triclinic
\[ \alpha \neq \beta \neq \gamma \]
\[ a \neq b \neq c \]

Orthorhombic
\[ \alpha = \beta = \gamma = 90^\circ \]
\[ a \neq b \neq c \]
Tetragonal
\[ \alpha = \beta = \gamma = 90^\circ \quad a_1 = a_2 \neq c \]

Hexagonal
\[ \alpha = \beta = 90^\circ \quad \gamma = 120^\circ \quad a_1 = a_2 \neq c \]

Rhombohedral
\[ \alpha = \beta = \gamma \neq 90^\circ \quad a_1 = a_2 = a_3 \]
a.k.a. Trigonal

Isometric
\[ \alpha = \beta = \gamma = 90^\circ \quad a_1 = a_2 = a_3 \]
<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Crystal Systems</th>
<th>Number of Lattice Points per Cell</th>
<th>Unit Cell and Lattice Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>primitive</td>
<td>$23P$</td>
<td>cubic</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4P$</td>
<td>tetragonal</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$222P$</td>
<td>orthorhombic</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$6P$ or $6C$</td>
<td>hexagonal</td>
<td>1 or 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2P$</td>
<td>monoclinic</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1P$</td>
<td>triclinic</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>body-centered</td>
<td>$23I$</td>
<td>cubic</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4I$</td>
<td>tetragonal</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$222I$</td>
<td>orthorhombic</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2I$</td>
<td>monoclinic</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>face-centered</td>
<td>$23F$</td>
<td>cubic</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$222F$</td>
<td>orthorhombic</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>end-centered</td>
<td>$222A$ or $222B$ or $222C$</td>
<td>orthorhombic</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>rhombohedral</td>
<td>$3R$</td>
<td>hexagonal</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
3-D Space

• Possible translations of a lattice point yield the 6 crystal class shapes by ‘moving’ a point in space (a, b, c or x, y, z coordinates)

• Those ‘movements’ have to preserve the symmetry elements and are thus limited in the number of possible shapes they will create.
Symmetry operators, again… but we save the last ones for a reason

- Must now define 2 more types of symmetry operators – Space group operators
- Glide Plane
- Screw Axes
- These are combinations of simple translation and mirror planes or rotational axes.
Glide Planes

• Combine translation with a mirror plane

• 3 different types:
  – Axial glide plane \((a, b, c)\)
  – Diagonal glide plane \((n)\)
  – Diamond glide plane \((d)\)

Diagonal and diamond glides are truly 3-D…
Screw Axes

• Combine translation with a rotation
• Can have 2, 3, 4, or 6-fold rotation (360°/n) and translation of some magnitude (rational fraction) of t (unit cell edge length)
• Subscripts indicate the magnitude of translation
  – 4_2 indicates a 4-fold axis translated every 2/4 t
  – 4_3 indicates a 4-fold axis translated every 3/4 t
  – 4 indicates a 4-fold axis translated every t
• The screw axes can be either right-handed (advances away from observer when rotated clockwise) or left-handed (advances away from observer when rotated counterclockwise)
Space Groups

• Atomic structure → Point groups (32 3-D symmetry combinations) + lattice type (the 14 different Bravais lattices) + glide planes + screw axes = 230 space groups

• They are represented:
  – Start with lattice type (P, I, F, R, A, B, or C) then symmetry notation similar to what we saw for point groups, but including the glides and screw axes
  – Garnet space group I4₁/a32/d
Internal – External Order

- We described symmetry of crystal habit (32 point groups)
- We also looked at internal ordering of atoms in 3-D structure (230 space groups)
- How are they different? – Remember that the internal order is always equal or greater than the external order
- All minerals fall into one of 6 crystal systems, one of 14 Bravais Lattices (variations of those systems based on 3-D assembly)
Mineral ID information

• Chapter 14

• Information to identify minerals:
  – Physical
  – Chemical
  – Optical
  – Crystallographic

have been reported. Associated minerals include garnet, sillimanite, spinel, plagioclase, anthophyllite, and orthopyroxene.

Varieties
A high-temperature polymorph of cordierite, indialite, is isostructural with beryl.

Related Minerals
Cordierite is structurally similar to beryl, and is chemically and structurally similar to osmumilite, (K,Na) (Fe,Mg)_{2}[(Al,Fe)]_{3}(Si,Al)_{12}O_{30} \cdot H_{2}O.

SHEET SILICATES
Serpentine Group Minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>antigorite</td>
<td>Mg_{6}Si_{4}O_{10}(OH)_{8}</td>
</tr>
<tr>
<td>chrysotile</td>
<td>Mg_{6}Si_{4}O_{10}(OH)_{8}</td>
</tr>
<tr>
<td>lizardite</td>
<td>Mg_{6}Si_{4}O_{10}(OH)_{8}</td>
</tr>
</tbody>
</table>

Antigorite, chrysotile, and lizardite comprise the serpentine group. Antigorite and lizardite are typically massive and fine grained; chrysotile is fibrous and is one of the few asbestiform minerals. Most of the world’s asbestos is chrysotile; crocidolite and amosite, both amphibole varieties, account for the rest. Chrysotile and lizardite are true polymorphs, but antigorite has a slightly different composition not reflected in its formula. Figures 3.5c and 14.6 show typical massive serpentine.

Crystallography
Monoclinic, \( a = 5.32 \), \( b = 9.50 \), \( c = 14.9 \), \( \beta = 101.9^\circ \), \( Z = 4 \); space group \( C2/m \); point group \( 2/m \).

Habit
Antigorite is commonly fine grained, massive, or platy, in contrast with fibrous chrysotile.

Structure and Composition
The layered structure consists of paired sheets of SiO_{4} tetrahedra and Mg(OH)_{6} octahedra stacked on top of each other (Figure 13.15). Antigorite has a slightly different composition from that indicated by its formula because the ratio of brucite layers to tetrahedral layers is slightly greater than 1. Because atoms in the tetrahedral and octahedral layers have slightly mismatched spacings, layers curve slightly. In antigorite the sheets curve in both directions, alternating on a fine scale, so the overall structure retains sheetlike properties. Small amounts of Ni, Mn, Al, Ti, and Fe typically substitute for Mg.

Occurrence and Associations
Antigorite is a common secondary mineral in mafic and ultramafic igneous rocks. It is also found in some marbles. In some serpentinides it is the only mineral present. Associated minerals include magnesium silicates, carbonates, hydroxides, and oxides, as well as olivine, pyroxene, amphibole, magnetite, spinel, chromite, magnetite, brucite, and talc.

Varieties
Garnierite is a Ni-rich variety of serpentine associated with Ni-peridotites.

Related Minerals
Antigorite is closely related to lizardite and chrysotile (common asbestos). Glaucophane, FeSi_{3}O_{10}(OH)_{4}, the Fe equivalent of serpentine, has a different structure.

Chrysotile

Origin of Name
From the Greek chrysos and tilos, meaning “golden” and “fiber.”

Hand Specimen Identification
Fiberlike, asbestiform appearance is diagnostic (Figures 3.5c and 14.6). Chrysotile may be distinguished from most fibrous amphiboles by its greenish white color; compare Plates 3.4 and 3.7.

Physical Properties
- Hardness: 3–5
- Specific gravity: 2.5–2.6
- Cleavage/fracture: none/uneven
- Luster/Transparency: greasy, waxy/translucent
- Color: variable white, greenish white
- Streak: white
Why did we go through all this?

- Lattice types and space groups are important in describing the arrangement of atoms in space.
- These arrangements result in planes of atoms which are spaced at defined intervals, controlled by the mineral structure, which is described by crystallography.
- They describe possible planes in crystalline structures where ions are aligned. Light and high-energy particles interact with those planes, which yield powerful diagnostic tools!
How does that translate to what we see??

- When a mineral grows in unrestricted space, we see the external order – the crystal habit
- When a mineral breaks, what defines where it is likely to break??