Mineral Physics 1: Earth Mineralogy and Phase Diagrams

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Outline

1. Basic Compositional Constraints
2. Building Minerals
3. Coordination environments
4. Substitution Mechanisms
5. Two Component Phase Diagrams, including Partial Melting
6. Additional slides on single crystal elasticity, composites, and thermal equations of state
Compositional constraints for Earth’s interior

- Solar atmospheric analyses

- Mineralogy and (isotope) geochemistry
  - Drill cores, mantle xenoliths, meteorites

- Going deeper
  - Geophysical observations, seismology, gravity
  - Extreme conditions: theory and experiments

Kola Superdeep Borehole
12.262 km (Kola 1989)

- Diamond-anvil cells
# Earth Chemistry (in general)

<table>
<thead>
<tr>
<th>Element Name</th>
<th>Symbol</th>
<th>Weight% crust</th>
<th>Weight% Whole Earth (approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>O²⁻</td>
<td>45.2</td>
<td>30</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si⁴⁺</td>
<td>27.2</td>
<td>15</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al³⁺</td>
<td>8.0</td>
<td>1</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe⁰,²⁺,³⁺</td>
<td>5.8</td>
<td>34.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca²⁺</td>
<td>5.1</td>
<td>1</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg²⁺</td>
<td>2.8</td>
<td>12.5</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na⁺</td>
<td>3.2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Potassium</td>
<td>K⁺</td>
<td>1.7</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni²⁺</td>
<td>&lt;1</td>
<td>4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>&lt;1</td>
<td>2</td>
</tr>
</tbody>
</table>

Where these elements reside dictates elastic and transport properties.
Abundance of the major minerals on the surface of the Earth (crust)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plagioclase</td>
<td>40%</td>
</tr>
<tr>
<td>Alkali feldspars</td>
<td>13%</td>
</tr>
<tr>
<td>Quartz</td>
<td>13%</td>
</tr>
<tr>
<td>Pyroxenes</td>
<td>11%</td>
</tr>
<tr>
<td>Nesosilicates</td>
<td>8%</td>
</tr>
<tr>
<td>Amphiboles</td>
<td>5%</td>
</tr>
<tr>
<td>Micas</td>
<td>5%</td>
</tr>
<tr>
<td>Clays</td>
<td>5%</td>
</tr>
</tbody>
</table>

Role of atomic structure:
- **Solids: crystalline vs. amorphous**
  Regular array of atoms lowers the system's energy.
  Competition between attractive (binding) and repulsive (electrostatic) forces.

- **Structure plays a major role in determining physical properties of materials.**

  **Determination:** X-ray and neutron diffraction, *ab initio* (bulk). TEM, EBSD, AFM (surface).

- **Deviations:** perfect crystals do not exist. Many key properties depend on deviations: defects (exception = silicon), phonons (lattice vibrations, atoms are moving, no single lattice at any given instant), surface (finite size effects).
Common Coordination Environments

Coordination number (CN) = # of nearest neighbors

- Linear (CN=2)
- Triangular (CN=3)
- Tetrahedral (CN=4)
- Octahedral (CN=6)
- Cubic (CN=8)
Common Coordination Environments

3-fold

Triangular

Triangular (CN=3)

\[
\begin{bmatrix}
\text{Ca}^{2+}
\end{bmatrix}
\begin{bmatrix}
\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array} \\
\begin{array}{c}
\text{C} \\
\text{O}
\end{array}
\end{bmatrix}
\]^{2-}

Calcite

(CaCO_3)
Common Coordination Environments

4-fold
Tetrahedral

Tetrahedral (CN=4)

\[
\begin{array}{c}
\text{O}^- \\
\text{Si} \\
\text{O}^- \\
\text{O}^-
\end{array}
\]

Quartz (SiO\textsubscript{2})
Common Coordination Environments

Octahedral (CN=6)

Periclase (MgO) (NaCl structure)

www.theochem.unito.it
Silicate classification, based on connectivity

Nesosilicates:
- Olivine
- Garnets

Sorosilicates:
- Hemimorphite

Cyclosilicates:
- Beryl

Inosilicates:
- Pyroxenes
- Amphibole

Inosilicates:
- Pyroxenes

Phyllosilicates:
- Micas \((\text{Si}_2\text{O}_5)^{2-}\)

Tectosilicates:
- Quartz, Feldspars


diagram of silicate structures
Unit Cells

• There are 7 lattice systems

• The lattice systems are characterized by the relative lengths of the cell edges \((a, b, c)\) and the angles between them \((\alpha, \beta, \gamma)\)

• These lattice systems can be further subdivided into 14 Bravais lattices
Cubic Lattice System

P
primitive
“simple cubic”

I
body-centered
“bcc”

F
face-centered
“fcc”

\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

made by Baszoetekouw at en.wikipedia
Primitive Cubic (Simple Cubic)
Primitive Cubic (Simple Cubic)

Very rare in metals (not efficient).
Example: Polonium metal.

Minerals with more than one atom type can have the primitive cubic structure.

Example: cesium chloride

Priming Cubic (Simple Cubic)
Body Centered Cubic

Many metals have the BCC structure: iron, lithium, sodium, potassium, chromium, barium, vanadium.
Face Centered Cubic

Halite – NaCl (fcc)

Face Centered Cubic

Sphalerite - (Zn,Fe)S
(fcc)

http://www.edmar-co.com/adriano/field/Trona/trona.html
Periclase-Wüstite Solid Solution

MgO \quad (\text{Mg}_{0.5}\text{Fe}_{0.5})\text{O} \quad \text{FeO}

“ferropericlase”

“magnesiowüstite”

B1 phase

Fm\bar{3}m

wüstite

periclase
Tetragonal Lattice System

P
primitive  “simple tetragonal”

I
body-centered  “centered tetragonal”

\[ a = b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]
Example of Tetragonal Lattice

http://www.minfind.com/mfthumbs

Rutile – TiO$_2$
Orthorhombic Lattice System

- **P** (primitive)
- **I** (body-centered)
- **A, B, C** (base-centered)
- **F** (face-centered)

\[ a \neq b \neq c \]

\[ \alpha = \beta = \gamma = 90^0 \]
Example of Orthorhombic Lattice

Olivine – Mg$_2$SiO$_4$
Rhombohedral Lattice System

\[ a = b = c \]
\[ \alpha = \beta = \gamma \neq 90^0 \]

The rhombohedral lattice is combined with the hexagonal lattice, grouped under the hexagonal family because the same hexagonal unit cell can be used for both.
Example of Rhombohedral Lattice

Calcite – CaCO$_3$

http://geophysics.ou.edu/geol1114/notes/minerals/calcite.jpg  
http://igs.indiana.edu/images/rocksandminerals/CalciteArticle_Figure2.jpg
**Monoclinic Lattice System**

- **P** (primitive)
- **C** (base-centered)

$a \neq b \neq c$

$\alpha = \gamma$, $\beta \neq 90^0$
Monoclinic Lattice System

**Diopside-hedenbergite**

$\text{Ca(Mg,Fe)Si}_2\text{O}_6$

**Orthoclase**

$\text{KAlSi}_3\text{O}_8$
Pyroxenes

Diopside  
*CaMg-pyroxene*

Enstatite  
*Mg-pyroxene*

Hedenbergite  
*CaFe-pyroxene*

Ferrosilite  
*Fe-pyroxene*

Photo by Rob Lavinsky

Photo by Stephan Wolfried

Photo by John Betts
Triclinic Lattice System

P
primitive

\[ a \neq b \neq c \]
\[ \alpha \neq \beta \neq \gamma \neq 90^\circ \]

Example: Labradorite, \((\text{Ca,Na})\text{Al}_2\text{Si}_2\text{O}_8\)
\[ \text{Ca}/(\text{Ca} + \text{Na}) = 50 - 70\% \]

Plagioclase (feldspar)

http://www.whitelotusmagazine.com/
Hexagonal Lattice System

$\gamma = 120^\circ$

$a = b \neq c$

$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

P primitive
Example of Hexagonal Lattice

Quartz – SiO$_2$

http://img.wikinut.com/img/2d94qwjwf6qf4xq/jpeg/0/Clear-Quartz-Point.jpeg
Hexagonal Close Packing compared with Face-Centered Close Packing
Hexagonal Close-Packing (HCP)

Beryllium, magnesium, zinc, cadmium, titanium metals. *Iron at large compressions*
Packing – HCP vs. FCC

HCP

ABA hexagonal close packed

FCC

ABC face-centered cubic

Packing – HCP vs. FCC
Interstitial Sites

Pauling’s Rules

1) The Radius Ratio Rule
2) The Electrostatic Valency Principle
3) Sharing of Polyhedrons
4) Crystals Containing Different Cations
Pauling’s First Rule

“The Radius Ratio Rule”

Predict coordination with the radius ratio:

\[ \frac{R_{\text{Cation}}}{R_{\text{Anion}}} \]

Cations are generally smaller than anions so begin with maximum ratio = 1.0

**General Rule:** Only cations that are large enough to not “rattle” around in the interstices and small enough to fit into the site are accepted.
Pauling’s First Rule

“The Radius Ratio Rule”

Around every cation, a coordination polyhedron of anions forms, in which the cation-anion distance is determined by the radius sums and the coordination number is determined by the radius ratio.

Red cation is coordinated by 6 blue anions (4 in the plane, 1 above and 1 below). The stability limit here is at $r_C/r_A = 0.414$. 
<table>
<thead>
<tr>
<th>$R_{\text{cation}}/R_{\text{anion}}$</th>
<th>C.N.</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>12</td>
<td>Hexagonal or Cubic Closest Packing</td>
</tr>
<tr>
<td>1.0 - 0.732</td>
<td>8</td>
<td>Cubic</td>
</tr>
<tr>
<td>0.732 – 0.414</td>
<td>6</td>
<td>Octahedral</td>
</tr>
<tr>
<td>0.414 – 0.225</td>
<td>4</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>0.225 – 0.155</td>
<td>3</td>
<td>Triangular</td>
</tr>
<tr>
<td>&lt; 0.155</td>
<td>2</td>
<td>Linear</td>
</tr>
<tr>
<td>Ion</td>
<td>Coordination Number (C.N.)</td>
<td>Coordination Polyhedron</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>K⁺</td>
<td>8 – 12</td>
<td>cubic to closest</td>
</tr>
<tr>
<td>Na⁺</td>
<td>8 – 6</td>
<td>cubic to octahedral</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>8 – 6</td>
<td>octahedral</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ti⁴⁺</td>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>4</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>4</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>P⁵⁺</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>S⁶⁺</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>C⁴⁺</td>
<td>3</td>
<td>triangular</td>
</tr>
</tbody>
</table>
Pauling’s Second Rule

“The Electrostatic Valency Principle”

An ionic structure will be stable to the extent that the sum of the strengths of the electrostatic bonds that reach an ion equal the charge on that ion.

In other words, the bond valence of each ion should be approximately equal to its oxidation state.

\[
\frac{\text{electrostatic bond strength}}{\text{cation charge}} = \frac{\text{cation charge}}{\text{coordination number}}
\]

\[s = \frac{Z}{CN}\]
Pauling’s Third Rule

“Sharing of Polyhedron Corners, Edges and Faces”

Shared edges, and particularly faces of two anion polyhedra in a crystal structure decreases its stability.

Sharing faces means the cations are closer together $\rightarrow$ less stable (cation-cation repulsion).

Sharing corners means the cations are further apart $\rightarrow$ more stable.
Pauling’s Fourth Rule

“In Crystals Containing Different Cations”

In a crystal containing different cations, those with large valence and small CN tend not to share polyhedron elements with each other.

(Sharing polyhedra with cations of high charge will place cations close together so that they repel.)

Olivine - \((\text{Mg,Fe})_2\text{SiO}_4\)

- Isolated \(\text{SiO}_4\) tetrahedra
  - small CN (4)
  - large valence (4)
- Contains both \(\text{Mg}^{2+}\) and \(\text{Fe}^{2+}\)
### Cations of Similar Sizes

#### K$^{1+}$
- 1.38 Å

#### Na$^{1+}$
- 1.02 Å

#### Ca$^{2+}$
- 1.00 Å

#### Mn$^{2+}$
- 0.83 Å

#### Fe$^{2+}$
- 0.78 Å

#### Mg$^{2+}$
- 0.72 Å

#### Fe$^{3+}$
- 0.65 Å

### Feldspars!
- Orthoclase, $\text{KAlSi}_3\text{O}_8$
- Albite, $\text{NaAlSi}_3\text{O}_8$
- Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$

### Double carbonates!
- Dolomite, $\text{CaMg(CO}_3)\text{2}$
- Ankerite, $\text{CaFe(CO}_3)\text{2}$
- Kutnohorite, $\text{CaMn(CO}_3)\text{2}$

Al$^{3+}$ substitutes for Si$^{4+}$ in silicates. C$^{4+}$ is the Si$^{4+}$ analog in carbonates, except that it forms triangular groups instead of tetrahedra.
Effect of Charge on Anion Size

(Sulfur has many oxidation states.)
Effect of Pressure

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Depth</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 GPa</td>
<td>crust</td>
<td>tetrahedral (4)</td>
</tr>
<tr>
<td>15 GPa</td>
<td>410 km</td>
<td>octahedral (6)</td>
</tr>
<tr>
<td>25 GPa</td>
<td>660 km</td>
<td>cubic (8)</td>
</tr>
</tbody>
</table>

A. Kavner
Goldschmidt’s Rules

1. Ions of similar size can extensively substitute for each other in an ionic crystal. If size difference is

- < 15%: free substitution
- 15 - 30%: limited substitution
- > 30%: little to no substitution
Goldschmidt’s Rules

2. Ions whose charges differ by one unit substitute readily for one another, as long as electrical neutrality of the crystal is maintained.

If the charges differ by more than one unit, substitution is generally slight.

\[
\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} : \text{very common}
\]

\[
\text{Na}^+ \leftrightarrow \text{Al}^{3+} : \text{extremely unlikely!}
\]
Goldschmidt’s Rules

3. Ions with higher ionic potential form a stronger bond with surrounding anions.

Ionic potential = ratio of electric charge to the radius of an ion.

Thus, for ions of similar radii but different charges, the ion with the higher charge enters the crystal preferentially.
Ringwood’s Modification of Goldshmidt’s Rules (1955)

4. Substitutions may be limited, even when the size and charge criteria are satisfied, when the competing ions have different electronegativities and form bonds of different ionic character.

For example, Na\(^+\) and Cu\(^+\) have the same radius and charge, but do not substitute for one another.
Effect of Temperature

At ambient conditions, Na\(^+\) and K\(^+\) don’t substitute for each other (ion difference of 25%), but at high temperatures, they will.

- Example: Alkali feldspars
- Degree of substitution gives us info about temperature of crystallization!

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(^{1+})</td>
<td>1.38</td>
</tr>
<tr>
<td>Na(^{1+})</td>
<td>1.02</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1.00</td>
</tr>
</tbody>
</table>

_Feldspars_
Orthoclase, \textbf{KAISi_3O_8}
Albite, \textbf{NaAlSi_3O_8}
Anorthite, \textbf{CaAl_2Si_2O_8}
Simple Substitution

Cations with identical charges:

\[
\text{Mg}^{2+} \leftrightarrow \text{Fe}^{2+}
\]

Periclase-wüstite solid solution:

\[
\text{MgO} \quad \rightarrow \quad (\text{Mg,Fe})\text{O} \quad \rightarrow \quad \text{FeO}
\]

periclase \quad \rightarrow \quad \text{wustite}

Olivine solid solution:

\[
\text{Mg}_2\text{SiO}_4 \quad \rightarrow \quad (\text{Mg,Fe})_2\text{SiO}_4 \quad \rightarrow \quad \text{Fe}_2\text{SiO}_4
\]

forsterite \quad \rightarrow \quad \text{fayalite}
Coupled Substitution

Substitute atoms of different charges by coupling atoms that increase charge with those that reduce it.

Plagioclase feldspar solid solution series:

\[
\text{Ca}^{2+} + \text{Al}^{3+} \leftrightarrow \text{Na}^{+} + \text{Si}^{4+}
\]

Ca\text{Al}_2\text{Si}_2\text{O}_8 \quad \text{albite}

Ca\text{Al}_2\text{Si}_2\text{O}_8 \quad \text{anorthite}

Ca\text{ }^{2+} \text{ and Na}^{+} \text{ occupy a distorted 8-fold coordination}

\text{Al}^{3+} \text{ and Si}^{4+} \text{ are tetrahedrally coordinated}
Coupled Substitution

Corundum – Ilmenite solid solution:

\[ 2\text{Al}^{3+} \leftrightarrow \text{Fe}^{2+} + \text{Ti}^{4+} \]
Omission Substitution

Substitute atoms of different charges and leave a site vacant, maintaining charge balance.

\[(n+1)M^{n+} \leftrightarrow nM^{(n+1)+} + \square\]

\[3Fe^{2+} \leftrightarrow 2Fe^{3+} + \square\]

Pyrrhotite:

Fe\(^{2+}\)S 
ferrous pyrrhotite 

\((Fe^{2+}_{0.7}Fe^{3+}_{0.2})\square_{0.1}S\) 
pyrrhotite with max Fe\(^{3+}\)
Omission Substitution

Chemical formulas for pyrrhotite:

$$(\text{Fe}^{2+}_{(1-3x)}\text{Fe}^{3+}_{2x}) \square_x \text{S}$$

or $\text{Fe}_{(1-x)}\text{S}$ ($x = 0$ to $0.2$)
Interstitial Substitution

Charge balance is maintained by placing ions in sites that are normally vacant.

Beryl (Al$_2$Be$_3$Si$_6$O$_{18}$) is made of rings of silicon tetrahedra, creating channels.
Interstitial Substitution

Monovalent cations can be inserted into these cavities.

\[ \square + \text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + (\text{K}^+, \text{Rb}^+, \text{Cs}^+) \]

\[ \square + \text{Si}^{4+} \leftrightarrow \text{Be}^{2+} + 2(\text{K}^+, \text{Rb}^+, \text{Cs}^+) \]
Two phases: plagioclase crystal (orange) and melt (blue)

The two phases (liquid and crystal) coexist in the white region

Two components: NaAlSi$_3$O$_8$ and CaAl$_2$Si$_2$O$_8$
Complete miscibility (mixability) in both liquid (magma) and crystal phases.

The following terms will be used synonymously:
1) liquid, melt and magma
2) solid, crystal and plagioclase
Pure albite melts at 1118° C

Pure anorthite melts at 1553° C
2-C Solid Solution Phase Diagram

Pure albite melts at 1118° C

Pure anorthite melts at 1553° C
Pure albite melts at 1118° C.

Pure anorthite melts at 1553° C.

Non endmembers do not have one melting temperature – they melt over a range of temperatures.
Solidus = line that separates all solid from liquid + solid
Solidus = line that separates all solid from liquid + solid

Liquidus = line that separates all liquid from liquid + solid
2-C Solid Solution Phase Diagram

Use the **liquidus** to determine the composition of the **melt**.

→ The melt is 15% anorthite.

Use the **solidus** to determine the composition of the **crystal**.

→ The crystal is 55% anorthite.
2-C Solid Solution Phase Diagram

The Lever Rule

Melt fraction:
\[ \frac{B}{A+B} = \frac{25}{15+25} = \frac{25}{40} = 0.625 \]

Crystal fraction:
\[ \frac{A}{A+B} = \frac{15}{15+25} = \frac{15}{40} = 0.375 \]

B decreases while A increases as we decrease T.

\( \text{NaAlSi}_3\text{O}_8 \)  Albite  % Anorthite  \( \text{CaAl}_2\text{Si}_2\text{O}_8 \)  Anorthite

Temperature (°C)

1600  liquid
1553  liquidus
1500  liquid and crystal
1400  solidus
1300
1200
1118
1000
900
800
700
600
500
400
300
200
100
0
Equilibrium vs. Fractional Melting

There are 2 ways to melt the mantle:

1) Equilibrium melting
   occurs when the solid and liquid phases are kept together as melting progresses

2) Fractional melting
   occurs if the liquid is removed from the solid as the solid melts
Equilibrium vs. Fractional Crystallization

There are 2 ways to crystallize solids from melt:

1) **Equilibrium crystallization**
   
   occurs when the solid and liquid phases are kept together as crystallization progresses

2) **Fractional crystallization**
   
   occurs if the solid is removed from the liquid as it crystallizes
Equilibrium Crystallization

Dark colors = more anorthite rich.
Light colors = more albite rich.

magma chamber

NaAlSi$_3$O$_8$  Albite
CaAl$_2$Si$_2$O$_8$  Anorthite

% Anorthite
Equilibrium Crystallization

magma chamber

Temperature (°C)

liquid

liquid and crystal

solidus

plagioclase

NaAlSi$_3$O$_8$
Albite

% Anorthite

CaAl$_2$Si$_2$O$_8$
Anorthite

Equilibrium Crystallization
Equilibrium Crystallization

These crystals are 80% Anorthite.

This melt is 47% Anorthite.

These crystals are 80% Anorthite.
Equilibrium Crystallization

These crystals are 80% An.

This melt is 47% An.

Melt vs. Crystal:
(70 - 47) / 33
23 / 33 = 70%
70% crystals
30% melt

magma chamber
Equilibrium Crystallization

These crystals are 70% Anorthite.

This melt is 30% Anorthite.

magma chamber
Equilibrium Crystallization

These crystals are 70% An

magma chamber

These crystals are 70% Anorthite (CaAl2Si2O8). The diagram illustrates the equilibrium crystallization process in a magma chamber. The diagram shows the temperature (°C) on the y-axis and the percentage of Anorthite (% An) on the x-axis.

Key points:
- **Liquidus** and **Solidus** curves define the temperature range where liquid and crystals coexist.
- **Plagioclase** (NaAlSi3O8) and **Albite** (CaAl2Si2O8) phases are indicated.
- The magma chamber diagram highlights the crystallization process at different temperatures and compositions.
Example of fractional crystallization, where we will remove the crystals.

Fractional Crystallization

magma chamber
This first crystal is 90% An

This melt is 70% An

Fractional Crystallization

magma chamber

liquid

liquid and crystal

plagioclase

solidus

Temperature (°C)

% Anorthite

NaAlSi$_3$O$_8$
Albite

CaAl$_2$Si$_2$O$_8$
Anorthite

1553
Fractional Crystallization

This melt is 70% An

The 90% An crystal sinks

magma chamber

liquid

liquid and crystal

solidus

plagioclase

NaAlSi$_3$O$_8$
Albite

% Anorthite

CaAl$_2$Si$_2$O$_8$
Anorthite
Fractional Crystallization

These crystals are 80% An
This melt is 47% An

magma chamber

% Anorthite

NaAlSi$_3$O$_8$ Albite

CaAl$_2$Si$_2$O$_8$ Anorthite
Fractional Crystallization

This melt is 47% Anorthite (NaAlSi$_3$O$_8$) and these crystals are 80% Anorthite (CaAl$_2$Si$_2$O$_8$).

Melt vs. Crystal:

\[
\frac{70 - 47}{33} = \frac{23}{33} = 70\%
\]

70% crystals, 30% melt.

Magma chamber
Fractional Crystallization

Crystals sink!

Liquidus

Solidus

Magma chamber

Temperature (°C)

NaAlSi$_3$O$_8$

Albite

% Anorthite

CaAl$_2$Si$_2$O$_8$

Anorthite
Fractional Crystallization

These crystals are 62% An.

This melt is 20% An.

magma chamber

% Anorthite
Fractional Crystallization

Melt vs. Crystal:
\[
\frac{47-20}{42} = \frac{27}{42} = 64\% \\
64\% \text{ crystals} \\
36\% \text{ melt}
\]

Magma chamber

Temperature (°C)

Liquid vs. Crystal

\[
\text{NaAlSi}_3\text{O}_8 \\
\text{Albite} \\
\text{CaAl}_2\text{Si}_2\text{O}_8 \\
\text{Anorthite}
\]

% Anorthite
Fractional Crystallization

Crystals sink!

magma chamber

Temperature (°C)

% Anorthite

NaAlSi$_3$O$_8$
Albite

CaAl$_2$Si$_2$O$_8$
Anorthite

plagioclase

liquid

solidus

liquid and crystal

1553
Fractional Crystallization

**Crystals:** 40% An  
**Melt:** 8% An  

Melt: 8% An  
Crystals: 40% An  

Magma chamber  

Temperature (°C)  

% Anorthite  

NaAlSi$_3$O$_8$  
Albite  

CaAl$_2$Si$_2$O$_8$  
Anorthite
Fractional Crystallization

Melt vs. Crystal: \( \frac{20-8}{32} \)
12/32 = 38%
38% crystals
62% melt

Magma chamber

NaAlSi_3O_8
Albite

CaAl_2Si_2O_8
Anorthite

Temperature (°C)

% Anorthite

Liquid vs. Crystal

1553
Fractional Crystallization

Crystals sink!

magma chamber

Temperature (°C)

0 10 20 30 40 50 60 70 80 90 100

% Anorthite

NaAlSi$_3$O$_8$
Albite

CaAl$_2$Si$_2$O$_8$
Anorthite

solidus

liquid

liquid and crystal

1553

1118
Fractional Crystallization

Last crystals are 8% Anorthite (CaAl$_2$Si$_2$O$_8$)

Magma chamber

Temperatures (°C):
- 1553°C
- 1600°C
- 1500°C
- 1400°C
- 1300°C
- 1200°C

Composition:
- NaAlSi$_3$O$_8$: Albite
- Anorthite (CaAl$_2$Si$_2$O$_8$)
Magma composition progressively changes as crystals are physically removed from the magma.
Bowen’s Reaction Series

High T
(1400°C)

Olivine → Orthopyroxene → Clinopyroxene → Amphibole → Biotite → Alkali feldspar → Muscovite → Quartz

1st to crystallize

Ca plagioclase → CaNa plagioclase → Na plagioclase

Ultramafic

Low T
(650°C)

Felsic

Last to crystallize
Fractional Crystallization

Palisades Sill (western shore of Hudson River, NJ)
Basaltic intrusion: 245–275 meters thick

Basalt cooled quickly at the edges of the intrusion.

**Diagram:**
- Sandstone
- Basalt
- Diorite
- Gabbro
- Olivine gabbro

**Mineralogical Characteristics:**
- Sodium-rich plagioclase feldspar; Fe-rich pyrox, hbl
- Calcium-rich plagioclase feldspar and pyroxene;
- Olivine, plag, pyrox

Fractional Crystallization

1200°C
Olivine

900°C
Pyroxene, Plagioclase feldspar

600°C
Plagioclase feldspar
Decompression Melting

Decompression melting of mantle peridotite to produce primary basaltic magmas.
Melting the Mantle

A: normal situation
B: mid-ocean ridge
C: hotspot (mantle plume)
D: island arc (subduction zone)

by Woudloper/Woodwalker geologist from Berne, Switzerland
Mantle Mineralogy
(Peridotitic)

Olivine
Pyroxenes
Garnets
Wadsleyite
Ringwoodite
Bridgmanite
Calcium silicate perovskite
Post-perovskite
D” Layer

Depth (km)

410
670
2600
2900

Volume fraction

0
1

Upper Mantle
Transition Zone
Lower Mantle

Tschauner et al. (2014)

Figure after J. Amodeo; orthopyroxene from minerals.gps.caltech.edu; olivine by Rob Lavinsky; wadsleyite by T. Kawazoe; ringwoodite by Joe Smyth
After Fei and Bertka, 1999, olivine $\rightarrow$ wadsleyite $\rightarrow$ ringwoodite $\rightarrow$ (bridgmanite+periclase) 

(Mg,Fe)$_2$SiO$_4$

$\text{Mg}_2\text{SiO}_4$

$\text{Br} + \text{Mw}$

$2\text{Mw} + \text{St}$

$\gamma + 2\text{Mw} + \text{St}$

$\alpha + \gamma$

Wadsleyite ($\beta$)

Ringwoodite ($\gamma$)

Olivine ($\alpha$)

$T=1600 \, ^\circ\text{C}$

Bridgmanite $\text{MgSiO}_3$

$\text{MgO} + \text{Mg}$

Ringwoodite ($\gamma$)

Wadsleyite ($\beta$)

Olivine ($\alpha$)

Liquid

Temperature ($^\circ\text{C}$)
Phase transitions in the \((\text{Mg,Fe})_2\text{SiO}_4\) system and relationship to seismic discontinuities

Review article: Frost, Elements (2008); Shim et al. (2001)
MgSiO$_3$ : enstatite $\rightarrow$ (majorite/akimotoite) $\rightarrow$ bridgmanite
Effect of majorite on the width & iron-partitioning of wadsleyite's phase transition

after Fei and Bertka, 1999
Phase diagram of a peridotitic mantle

Computed from first principles

Stixrude & Lithgow-Bertelloni (2011)
Effect of hydroxyl (OH)^- on olivine’s phase transition

(after Frost (2008))
Phase transitions in upper mantle mineral assemblages

Figure modified from Fei and Bertka (1999) and Liu, L., and Bassett, W.A. (1986).

**Exact chemistry of these minerals depends on phase equilibrium**
The upper mantle discontinuities

1. Temperature: decreases transition pressure ($\alpha, \beta$)

2. Presence of iron affects:
   * width of transition (increases)
   * transition pressure (typically decreases)

3. Presence of garnet affects:
   * width (decreases, because of iron exchange)
   * transition pressure (increases, because of aluminum)
   * Clapeyron slope ($dP/dT$) (changes sign, from neg. to pos.)

4. Adding OH to the system:
   * Decreases transition $P$
   * Widens the transition
Cross Section of Earth

- **Upper mantle**: ~5 to 20% reduction in $V_p$
- **Transition zone**: ~10 to 30% reduction in $V_s$
- **Lower mantle**: ~4 to 14% denser
- **D” layer**: $V_p/V_s$ range ~1 to 5

**ULVZs**
- 5-60 km thick
- ~5 to 20% reduction in $V_p$
- ~10 to 30% reduction in $V_s$
- ~4 to 14% denser
- $V_p/V_s$ range ~1 to 5

---

Garnero and Helmberger (1996); Lay et al. (1998); Rost et al. (2005), Idehara et al. (2007), Idehara (2011); Thorne and Garnero (2004)
Periclase-Wüstite Solid Solution

Periclase remains in the rocksalt (B1) structure throughout lower mantle pressures.

Wüstite experiences a rhombohedral distortion around 17 GPa.
Spin Pairing in Octahedral Fe$^{2+}$

Jahn–Teller distortion

energy

high spin

t$_{2g}$

eg

spin transition pressure

spin pairing energy

crystal field splitting energy

symmetric charge distribution

low spin

t$_{2g}$

eg

3d-electron pseudocharge densities from Tsuchiya et al., PRL 96 (2006)
A Systematic Study

• Fit a spin crossover equation of state to previous pressure-volume data sets for compositions ranging from 10-60 mol% FeO, using either a neon pressure medium or laser-annealed ionic thermal insulator medium.

• Compare resulting equation of state parameters.

• Directly compare to results from Mössbauer spectroscopy, which is sensitive to iron’s spin state.
X-ray Diffraction Patterns

Integrated x-ray diffraction patterns for Fp48 at 0, 15 and 46 GPa at 300 K.

Rhombohedral distortion results in peak splitting:

111 101
003

220 110
104

No peak splitting was observed.
Experimental Methods

- Low-spin iron has a smaller ionic radius than high-spin iron. Thus, low-spin (Mg,Fe)O has a smaller volume than high-spin (Mg,Fe)O.

- The electronic environment of low-spin iron is more symmetrical than that of high-spin iron.

X-ray Diffraction Experiments
- Observe volume change with pressure through the spin crossover region

Synchrotron Mössbauer Spectroscopy
- Direct access to the electronic environment of the iron atoms

Solomatova et al., Am. Min (2016)
Previous Experiments on (Mg,Fe)O

<table>
<thead>
<tr>
<th>FeO %</th>
<th>Methods</th>
<th>Pressure Mediums</th>
<th>Pressure Scales</th>
<th>Spin Transition Pressure</th>
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<tbody>
<tr>
<td>MgO</td>
<td>Conventional Mössbauer</td>
<td>None</td>
<td>Ruby</td>
<td>50% volume collapse</td>
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<td></td>
<td>X-ray emission</td>
<td>Boron epoxy</td>
<td>NaCl</td>
<td>50% low spin population</td>
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<tr>
<td></td>
<td>Powdered x-ray diffraction</td>
<td>NaCl</td>
<td>Pt</td>
<td>Spin pairing energy = crystal field splitting energy</td>
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<td>Single-crystal x-ray diffraction</td>
<td>KCl</td>
<td>Au</td>
<td>Visual inspection of data</td>
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<td></td>
<td>Synchrotron Mössbauer</td>
<td>Ar</td>
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<td></td>
<td>Optical absorption</td>
<td>Alcohol mixtures</td>
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<tr>
<td></td>
<td></td>
<td>Ne</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>He</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Spin Crossover Equation of State

48 mol% FeO

60 mol% FeO

17 mol% FeO

Unit cell volume ($\text{Å}^3$)

$V_0$ ($\text{Å}^3$)

Pressure (GPa)

$K_0$ (GPa)

F (GPa)

HS
TR
LS

Solomatova et al., Am. Min (2016)
Volume and Bulk Modulus of (Mg,Fe)O

Solomatova et al., Am. Min (2016)
Spin Transition Pressure and Width of (Mg,Fe)O

(Mg_{1-x}Fe_x)O with x=0.10 (Marquardt et al., 2009), x=0.17 (Lin et al., 2005), x=0.25 (Mao et al., 2011), x=0.35 (Chen et al., 2012), x=0.39 (Zhuravlev et al., 2010; Fei et al., 2007), x=0.48 (Solomatova et al. 2016), and x=0.60 (Lin et al., 2005). From Solomatova et al. (2016)
Spin Transition Width

- Core-mantle boundary temperatures: 
  - 3300–4300 K

- Spin transition width is expected to increase with temperature.

- Spin transition width is larger for higher Fe content.

- There will be a fraction of high-spin population (positively buoyant) at the core-mantle boundary.
Influence of the continuous spin crossover on mantle dynamics

- Advective heat transport more effective
- Spin density anomaly
  - Sturhahn, Jackson, Lin., GRL (2005)
  - First principles: e.g., Tsuchiya et al. (2006), Wentzcovitch et al. (2009)
- "Spin buoyancy"
  - Bower, Gurnis, Jackson, Sturhahn. GRL (2009)
- Adveective heat transport more effective
The core-mantle boundary region, D”

Seismic discovery that D” layer could be a distinct boundary: Sidorin et al. (1999); e.g., Helmberger et al. (2005); Hernlund et al. (2005); van der Hilst et al. (2007); dozens more since…

Bridgmanite \((Pbnm)\)  
\[
\text{MgSiO}_3
\]

Post-bridgmanite \((Cmcm)\)  
\[
\text{MgSiO}_3
\]

Murakami et al. (2004); Oganov & Ono (2004)
The Clapeyron slope \((dP/dT = dS/dV)\) of the bridgmanite to post-bridgmanite transition

Negative molar volume and enthalpy changes of 0.4 \(\text{cm}^3\ \text{mol}^{-1}\) and 11.8 \(\text{kJ} \text{ mol}^{-1}\) for the \(\text{Br}\) to \(\text{PBr}\) transition at 0 K stabilize the \(\text{PBr}\) at low temperatures and high-P. Vibrational entropies calculated favor \(\text{Br}\) with increasing temperatures (105.5 J K\(^{-1}\)mol\(^{-1}\) for \(\text{Br}\) vs. 99.2 J K\(^{-1}\)mol\(^{-1}\) for \(\text{PBr}\) at 298 K) (Stølen & Trønnes 2007).
The Clapeyron slope of the bridgmanite to post-bridgmanite transition affects its presence/absence in Earth, because the temperature may be variable and the transition pressure is very close to CMB pressures on Earth.

Implications for: phase relations, chemistry, and heat flow from the core

e.g., Hirose (2005); Lay et al., Science (2006); Monnereau & Yuen, PNAS (2007); Shim (2008)
Phase diagram of dense silica, SiO$_2$
Each phase has its distinct (an)isotropic properties
Temperature of CMB dictates phase equilibrium

Zhang et al. EPSL (2016)
Summary

1. Basic Compositional Constraints
2. Building Minerals
3. Substitution Mechanisms
   * Examples of minerals down to Earth's core
4. Two Component Phase Diagrams, including Partial Melting
   * Phase diagrams of mantle minerals
   * Spin crossover and width for (Mg,Fe)O
5. Each mineral will dictate differently the buoyancy, seismic wave speeds, thermal and electrical conduction, rheological behavior (flow). Collectively, assemblages can further be different
Slides on single crystal
elasticity, isotropic averaging,
and equations of state

Jennifer M. Jackson
Caltech
Hooke’s Law: \( \sigma_{ij} = C_{ijkl} \varepsilon_{kl} \)

\[
\begin{array}{ccccccccccc}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33} \\
\end{array}
\]

\[
\begin{array}{ccccccccccc}
C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1112} & C_{1113} & C_{1131} & C_{1121} \\
C_{2211} & C_{2222} & C_{2233} & C_{2212} & C_{2213} & C_{2223} & C_{2231} & C_{2211} \\
C_{3311} & C_{3322} & C_{3333} & C_{3312} & C_{3313} & C_{3323} & C_{3331} & C_{3311} \\
C_{2311} & C_{2322} & C_{2333} & & & & & & \\
C_{1311} & C_{1312} & C_{1313} & & & & & & \\
C_{1211} & C_{1212} & C_{1213} & & & & & & \\
C_{3211} & C_{3222} & C_{3233} & & & & & & \\
C_{3111} & C_{3122} & C_{3133} & & & & & & \\
C_{2111} & C_{2122} & C_{2133} & & & & & & \\
\end{array}
\]

One can fill in the empty spots of the tensor...

The single crystal elastic modulus tensor \( C_{ijkl} \) (4th rank) described the elastic energy density of a material. Hooke’s law describes the static elasticity.

One can see how the single crystal elastic modulus tensor \( C_{ijkl} \) can reduce from 81 elements to 36 elements

\[
\mu = \frac{\text{Shear Stress}}{\text{Shear Strain}}, \quad K = \frac{\text{Vol Stress}}{\text{Vol Strain}} = -V \frac{dP}{dV}, \quad \text{pressure} = -K \frac{\Delta V}{V}
\]
Form of the \((s_{ij})\) and \((c_{ij})\) matrices

**Key to notation**

- ● zero component
- ○ non-zero component
- • equal components
- ○ components numerically equal, but opposite in sign
- ○ twice the numerical equal of the heavy dot component to which it is joined (for \(s\))
- ○ the numerical equal of the heavy dot component to which it is joined (for \(c\))
- X \(2(s_{11}-s_{12})\) (for \(s\))
- X \(3/2(c_{11}-c_{12})\) (for \(c\))

All the matrices are symmetrical about the leading diagonal.

After Nye, 1959
Elastic waves in cubic crystals

Using Newton’s equations of motion of a unit volume element in a continuum medium:

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} = \vec{F}, \quad F_i = \sum_j \frac{\partial \sigma_{ij}}{\partial x_j}$$

\(\vec{u} =\) displacement  
\(\rho =\) specific mass  
\(\vec{F} =\) force that balances stress on a volume element

Christoffel equation: \(\sum_i \sum_j \sigma_{ij} a_j a_i - \rho V^2 \delta_{ik} = 0\)

Simple cases, 1) Longitudinal wave propagating in the \(x_1\) direction, displacement in “1” direction:

$$\rho \frac{\partial^2 u}{\partial t^2} = C_{11} \frac{\partial^2 u_1}{\partial x_1^2} \quad C_{11} = \rho V_{P[100]}^2$$

2) Shear wave propagating in the \(x_1\) direction, with particle displacement in the “2” direction:

$$\rho \frac{\partial^2 u}{\partial t^2} = C_{44} \frac{\partial^2 u_2}{\partial x_1^2} \quad C_{44} = \rho V_{SV,SH[100]}^2$$

More complex cases that highlight dynamics involving waves: waves in the [110] plane

$$\frac{1}{2} \left( C_{11} + C_{12} + C_{44} \right) = \rho V_{P[110]}^2, \quad C_{44} = \rho V_{SV[110]}^2, \quad \frac{1}{2} \left( C_{11} - C_{12} \right) = \rho V_{SH[110]}^2$$
Sound velocities in MgO
as a function of direction in (100) plane
at room temperature (blue) and 1500 K (red)
Single-crystal Elastic Moduli of MgO as a function of temperature

\[ C_{11}, C_{44}, C_{12} \]

- This study
- Sumino, 1983
- Isaak, 1989

Temperature, K

Sinogeikin et al. 2000
Aggregate Elastic Moduli in MgO as a function of temperature

![Graph showing Aggregate Elastic Moduli in MgO as a function of temperature](image-url)
Single-crystal elastic moduli (C<sub>ij</sub> s) of Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> orthoenstatite

Orthoenstatite crystal structure:

Orthoenstatite crystal structure:

- C<sub>22</sub>
- C<sub>33</sub>
- C<sub>23</sub> = C<sub>32</sub>
- C<sub>44</sub>

Propagation is along c, polarized in b-plane

C<sub>33</sub> = ρ(V<sub>P[001]</sub>)<sup>2</sup>
C<sub>55</sub> = ρ(V<sub>S[→c,a↑]</sub>)<sup>2</sup>
Single crystal anisotropy: Upper mantle

Depth (km)

Anisotropy (%)
Single crystal anisotropy: Transition zone and lower mantle

- Wadsleyite
- Ringwoodite
- Stishovite
- MgO
- Mg-Perovskite
- Calcium Chloride

Depth (km): 0, 10, 20, 30, 40, 50, 60, 670, 410, 520, 1170, 2230

Elastic properties of composite materials

- Starting point: single crystal elasticity
- Single crystal to polycrystalline aggregate of the same material
- Evaluate the boundary conditions of grain interaction

figure Phil Skemer
Voigt-Reuss-Hill bounds

• Obtaining aggregate elastic moduli (K, \(\mu\)) from \(C_{ij}\)'s: Voigt and Reuss elasticity bounds on aggregates of the same crystallites (Nye 1959):
  – Voigt = uniform strain (isostrain), given in terms of single-crystal stiffnesses, \(C_{ij}\)'s.
  – Reuss = uniform stress (isostress), given in terms of the inverse of single-crystal compliances, \(S_{ij}\)'s\(^{-1}\).
  – Voigt-Reuss-Hill = arithmetic average of Voigt and Reuss bounds.
    • Hill showed that the real value must be between these two bounds

• Compute the bounds for a monomineralic aggregate
## Elastic Tensors of Mg end-member Upper Mantle Minerals

<table>
<thead>
<tr>
<th></th>
<th>( \rho ) (g/cc)</th>
<th>( C_{11} ) (GPa)</th>
<th>( C_{22} ) (GPa)</th>
<th>( C_{33} ) (GPa)</th>
<th>( C_{44} ) (GPa)</th>
<th>( C_{55} ) (GPa)</th>
<th>( C_{66} ) (GPa)</th>
<th>( C_{12} ) (GPa)</th>
<th>( C_{13} ) (GPa)</th>
<th>( C_{23} ) (GPa)</th>
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</thead>
<tbody>
<tr>
<td>Gt, Py:</td>
<td>3.57</td>
<td>296</td>
<td>94</td>
<td>111</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Mg}_3\text{Al}_2\text{Si}<em>3\text{O}</em>{12} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ol, Fo:</td>
<td>3.22</td>
<td>328</td>
<td>200</td>
<td>235</td>
<td>67</td>
<td>81</td>
<td>81</td>
<td>69</td>
<td>69</td>
<td>73</td>
</tr>
<tr>
<td>( \text{Mg}_2\text{SiO}_4 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opx, Oe:</td>
<td>3.194</td>
<td>233</td>
<td>171</td>
<td>216</td>
<td>83</td>
<td>79</td>
<td>77</td>
<td>73</td>
<td>56</td>
<td>50</td>
</tr>
<tr>
<td>( \text{Mg}_2\text{Si}_2\text{O}_6 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cubic phases, such as garnet and periclasce:

\[
K_{S,R} = K_{S,V} \text{ (GPa)} = \frac{(C_{11} + 2C_{12})}{3}
\]

\[
\mu_V \text{ (GPa)} = \frac{1}{5}(C_{11} - C_{12} + 3C_{44})
\]

\[
\mu_R \text{ (GPa)} = 15\left[\frac{12}{(C_{11} - C_{12})} + \frac{9}{C_{44}}\right]
\]

\[
\sigma_{ij} = C_{ij} \varepsilon_{kl}
\]

\[
\varepsilon_{kl} = S_{ij} \sigma_{ij}
\]
Voigt-Reuss-Hill bounds
Orthorhombic

• Voigt = uniform strain (isostrain), given in terms of single-crystal stiffnesses, $C_{ij}$’s.
  – $9K_V = C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})$
  – $\mu_V = 1/15[(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{13} + C_{23}) + 3(C_{44} + C_{55} + C_{66})]$

• Reuss = uniform stress (isostress), given in terms of the inverse of single-crystal compliances, $S_{ij}$’s$^{-1}$.
  – $1/K_R = (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})$
  – $15/\mu_R = 4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})$

• Voigt-Reuss-Hill = arithmetic average of Voigt and Reuss bounds, applies to all symmetric classes.
  – $K_{VRH \text{ or } H} = \frac{1}{2}(K_V + K_R)$
  – $\mu_{VRH \text{ or } H} = \frac{1}{2}(\mu_V + \mu_R)$
### Aggregate Elastic Properties: Polymorphs (allotropes), isostructures, metals

<table>
<thead>
<tr>
<th></th>
<th>ρ (g/cc)</th>
<th>K&lt;sub&gt;S&lt;/sub&gt;,&lt;sub&gt;VRH&lt;/sub&gt; (GPa)</th>
<th>μ&lt;sub&gt;VRH&lt;/sub&gt; (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphite</td>
<td>2.26</td>
<td>160</td>
<td>109</td>
</tr>
<tr>
<td>diamond</td>
<td>3.5</td>
<td>443</td>
<td>536</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.16</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>MgO</td>
<td>3.58</td>
<td>160</td>
<td>130</td>
</tr>
<tr>
<td>α-Fe</td>
<td>7.87</td>
<td>167</td>
<td>82</td>
</tr>
</tbody>
</table>

![Structure of Diamond](image1.png)

![Structure of Graphite](image2.png)

![Covalent bond](image3.png)

![Carbon atom](image4.png)

![Weak bonding forces](image5.png)

![body centered cubic](image6.png)
Comparing Aggregate Elastic Properties of Polymorphs

<table>
<thead>
<tr>
<th>Crystal class/form</th>
<th>$\rho$ (g/cc)</th>
<th>$K_{S, \text{VRH}}$ (GPa)</th>
<th>$\mu_{\text{VRH}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSiO$_3$ isotropic/glass</td>
<td>2.76</td>
<td>79</td>
<td>31</td>
</tr>
<tr>
<td>Mg$_2$Si$_2$O$_6$ orthorhombic/orthoenstatite</td>
<td>3.194</td>
<td>107.6</td>
<td>76.8</td>
</tr>
<tr>
<td>MgSiO$_3$ Orthorhombic/bridgmanite</td>
<td>4.108</td>
<td>250</td>
<td>180</td>
</tr>
<tr>
<td>MgSiO$_3$ orthorhombic/post-bridgmanite</td>
<td>4.25</td>
<td>230</td>
<td>136</td>
</tr>
</tbody>
</table>
# Aggregate elastic properties of some major upper mantle minerals

<table>
<thead>
<tr>
<th></th>
<th>$\rho$ (g/cc)</th>
<th>$K_{S,V}$ (GPa)</th>
<th>$K_{S,R}$ (GPa)</th>
<th>$K_{S,\text{VRH}}$ (GPa)</th>
<th>$\mu_V$ (GPa)</th>
<th>$\mu_R$ (GPa)</th>
<th>$\mu_{\text{VRH}}$ (GPa)</th>
<th>$V_{P,\text{VRH}}$ (km/s)</th>
<th>$V_{S,\text{VRH}}$ (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Qt, Py:</strong> Mg$_3$Al$_2$Si$<em>3$O$</em>{12}$</td>
<td>3.57</td>
<td>172.7</td>
<td>172.7</td>
<td>172.7</td>
<td>92.2</td>
<td>92.2</td>
<td>92.2</td>
<td>9.09</td>
<td>5.08</td>
</tr>
<tr>
<td><strong>Ol, Fo:</strong> Mg$_2$SiO$_4$</td>
<td>3.22</td>
<td>132</td>
<td>127</td>
<td>129.5</td>
<td>82.6</td>
<td>79.6</td>
<td>81.1</td>
<td>8.59</td>
<td>5.02</td>
</tr>
<tr>
<td><strong>Opx, Oen:</strong> Mg$_2$Si$_2$O$_6$</td>
<td>3.19</td>
<td>108.6</td>
<td>106.6</td>
<td>107.6</td>
<td>77.2</td>
<td>76.4</td>
<td>76.8</td>
<td>8.11</td>
<td>4.90</td>
</tr>
</tbody>
</table>

Other important elastic properties:

$$V_F^2 = \left( \frac{K_S + \frac{4}{3} \mu}{\rho} \right)$$

$$V_S^2 = \frac{\mu}{\rho}$$

$$V_\phi^2 = \frac{K_S}{\rho} = \left( V_P^2 - \frac{4}{3} V_S^2 \right)$$

$$\nu = \frac{\left( \frac{V_P}{V_S} \right)^2 - 2}{2 \left[ \left( \frac{V_P}{V_S} \right)^2 - 1 \right]} = - \frac{\varepsilon_{22}}{\varepsilon_{11}}$$
Aggregate Sound Velocities in MgO as a function of temperature
Elasticity of composites made of heterogeneous materials

- Starting point: Aggregate isotropic properties of each component
- Add another component to the aggregate
- Compute V-R-H bounds for the multi-phase aggregate (rock)
- Calculate elastic properties of a multi-phase mixture (Watt et al. 1976):

\[
M^*_R = \left( \sum_{i=1}^{n} \frac{\nu_i}{M_i} \right)^{-1} \leq M^* \leq \sum_{i=1}^{n} \nu_i M_i = M^*_V
\]
Grüneisen parameter

• Synthesis between thermal and elastic properties, provides the physical basis for thermoelastic coupling.

• Thermoelastic coupling: Bulk modulus (section 2.3, JPP). Two intensive variables (T and stress) depend only on two extensive variables (S and strain). Hydrostatic pressure (geophysically relevant), the chain rule, and definitions of the adiabatic and isothermal bulk moduli (Table 1.2):

\[ K_S - K_T = \alpha K_T T \left( \frac{\alpha K_S V}{C_P} \right), \quad \gamma_{th} = \left( \frac{\alpha K_S V}{C_P} \right) = \left( \frac{\alpha K_S}{T} \right) \left( \frac{\partial T}{\partial P} \right)_S \]

• The Grüneisen parameter describes the increase in internal pressure, caused by heating a material at constant volume. It is the coefficient relating thermal pressure to thermal energy per unit volume:

\[ \Delta P_{th} = \gamma_{th} \left( \frac{\Delta U}{V} \right) \]
Phonon DOS for *hcp*-iron and the Grüneisen parameter

\[ \Delta P_{vib} = \gamma_{vib} \left( \frac{\Delta U_{vib}}{V} \right) \]

\[ \Delta P_{vib} \]

\[ \gamma_{vib} \]

\[ \gamma \]

\[ V \text{ (cm}^3 / \text{mol)} \]

Murphy et al. (GRL 2011; PEPI 2011); Murphy et al. (JGR 2013)
Approximations for vibrational energy (thermal pressure)

\[
P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F_{\text{elastic}}}{\partial V}\right)_T - \left(\frac{\partial F_{\text{phonon=vib}}}{\partial V}\right)_T
\]

- Approximations to the phonon (“vib”) part:
  - Debye approximation (1912):
    - Assumes all modes are acoustic: collapse DOS to one mode
    - Max. radius corresponds to max cut-off frequency: \( \omega_D = k_D v_D \)
    - Only considers monatomic case to determine \( k_D \)

\[
\frac{3}{v_D^3} = \frac{1}{v_p^3} + \frac{2}{v_s^3}
\]

\[
4/3 k_D^3 = (2\pi/a)^3
\]
Debye approximation for vibrational energy

\[ P_{\text{phonon=vibrational}} = F_{\text{vib}} = E_{\text{vib}} = \int_{0}^{\omega} \langle n \rangle \hbar \omega g(\omega) \, d\omega \]

- Assume 3D shape of Brillouin zone is spherical, with radius \( k_D \)

- Debye approximation to determine \( E_{\text{vib}} \):

\[
E_{\text{vib}} = 9nN_A k_B T x_D^{-3} \int_0^{x_D} x^3 / [\exp(x) - 1] \, dx, \quad \text{where}
\]

\[
x = \frac{\hbar \omega_D}{k_B T},
\]

\[
x_D = \frac{\theta_D}{T},
\]

\[
\theta_D = \frac{\hbar \omega_D}{k_B} = \text{“elastic Debye temperature”}
\]

\[
\text{DOS} = g(\omega) \approx B \omega_D^2 / \nu_D^3
\]
Phonon DOS for hcp-iron and the Grüneisen parameter

\[ \gamma_{\text{Debye}} = \frac{1}{3} + \left( \frac{\ln \left[ \left( \frac{1}{v_P^3} + \frac{2}{v_S^3} \right) / 3 \right]}{d \ln \rho} \right)^{-1/3} \]

\[ \gamma_{\text{vib}} q = 0.8 \]
\[ \gamma_{\text{vib}} q = 1.2 \]
\[ \gamma_{\text{pp}} q = 0.8 \]
\[ \gamma_{\text{pp}} q = 1.2 \]

Merkel et al. (2000)
Dewaele et al. (2006)
Sha and Cohen (2010)
Obtaining Total Thermal Pressure ($P_{th}$)

$$P_{th} = P_{vib} + P_{el} = -\left(\frac{\partial F_{vibrational}}{\partial V}\right)_T - \left(\frac{\partial F_{electronic}}{\partial V}\right)_T$$

- **Phonon density of states**: provides total vibrational free energy: $P_{th}$ and $\gamma_{th}$ through volume dependence of the DOS. Requires a measurement of the phonon density of states and an electronic term. Or, estimate from Debye model.

- **Shock wave data**: one uses the conservation of energy & momentum in a shock experiment to determine the thermal pressure in the shock. Requires, in part, knowing the pressure and temperature accurately.

- **Density Functional Theory calculations**: predicts the phonon and electronic density of states for a material at different volumes. Requires the correct “functional” for all atoms.

- **PVT Measurements**: Measure volume as a function of pressure and temperature, then fit your data to a Mie-Grüneisen EOS to obtain $P_{th}$ and $\gamma_{th}$. Less direct.
Perfect elastic material, independent of stress/strain: harmonic oscillatory

- $F=k(r-r_e)$, restoring force is proportional to elongation, and the symmetric interatomic pair potential (parabolic)


- The mean bond length becomes longer than the equilibrium value.
- Cause of thermal expansion, Mie's potential:
  \[ E(r) = -\frac{a}{r^m} + \frac{b}{r^n} \]
  - m: attractive force
  - n: repulsive force

Quasi-harmonic approximation: effect of T via volume change due to thermal expansion only, harmonic around around their new positions
Universal EoS

\[ P = -\left( \frac{\partial F}{\partial V} \right)_T = -\left( \frac{\partial F_{\text{elastic}}}{\partial V} \right)_T - \left( \frac{\partial F_{\text{phonon}=\text{vib}}}{\partial V} \right)_T - \left( \frac{\partial F_{\text{electronic, spin, etc}}}{\partial V} \right)_T \]

- Anything with a volume term creates a pressure
- Elastic (static)
  - Describes equilibrium positions of material after it has undergone, for example: finite strain (Birch-Murnaghan)
    - Elastic = zero-energy exchange
  - Shear elasticity
  - No information on energy from vibrations (phonons) or electrons
- Vibrational (Temperature > 0 kelvin), \( P_{\text{vib}} \)
  - No information on where the equilibrium positions are
  - Describes dynamics of the system given by the phonons (PDOS)
    - deviation from equilibrium positions
    - harmonic, anharmonic
- Electronic
  - Dynamics of electronic states, e.g., conduction bands (EDOS)