From thermodynamics to geodynamics: 
An overview of the geophysical thermodynamics 
of phase relations

Craig R. Bina

Dept. of Earth and Planetary Sciences 
Northwestern University 
Evanston, Illinois, U.S.A.

Katedra geofyziky 
Matematicko-fyzikální fakulta 
Univerzita Karlova v Praze 
přednášky na podzim 2011 
4. lekce 2.11.
The Plagioclase → Spinel → Garnet Lherzolite Transitions

**Facies:** plagioclase lherzolite → spinel lherzolite → garnet lherzolite

**Reaction 1:** plagioclase + olivine → spinel + pyroxenes

**Reaction 2:** spinel + pyroxenes → garnet + olivine

**Example 1:** \(\text{CaAl}_2\text{Si}_2\text{O}_8\) (plag) + 2 \(\text{Mg}_2\text{SiO}_4\) (olv) → 
\[\text{MgAl}_2\text{O}_4\] (sp) + \(\text{Mg}_2\text{Si}_2\text{O}_6\) (opx) + \(\text{CaMgSi}_2\text{O}_6\) (cpx)

**Example 2:** \(\text{MgAl}_2\text{O}_4\) (sp) + 1.55 \(\text{Mg}_2\text{Si}_2\text{O}_6\) (opx) + 0.45 \(\text{CaMgSi}_2\text{O}_6\) (cpx) → 0.85 \(\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}\) (gt) + 0.15 \(\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}\) (gt) + \(\text{Mg}_2\text{SiO}_4\) (olv)

**Summary 1:** sp, opx and cpx increase; plag vanishes; olv decreases

**Summary 2:** gt and olv increase; sp vanishes; opx and cpx decrease
plagioclase → spinel → garnet
lherzolite transitions

(a) Comparison of observed ocean depths with those predicted for a conductively cooled plate ($t^{1/2}$ curve). (b) Temperature-depth profiles for pure conductive cooling (equation (1)) with thermal diffusivity of $8 \times 10^{-3}$ cm$^2$/s and maximum temperature of 1350°C.

(Figure 1 of Wood and Yuen, 1983)
Experimental and calculated $P-T$ boundaries for the spinel lherzolite-garnet lherzolite reaction. Note calculated change in sign of the $P-T$ slope with decreasing temperature.
spinel → garnet lherzolite transition

At very low temperatures:

\[ \text{MgAl}_2\text{O}_4 + 1.55 \text{Mg}_2\text{Si}_2\text{O}_6 + 0.45 \text{CaMgSi}_2\text{O}_6 \rightarrow \]

spinel enstatite (opx) diopside (cpx)

↓ (increasing P)

\[ 0.85 \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 0.15 \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Mg}_2\text{SiO}_4 \rightarrow \]

garnet solid solution (pyrope + grossular) olivine

Reactants are nearly pure phases, but products contain garnet solid solution:

\[ (\text{Mg}_{0.85}\text{Ca}_{0.15})_3\text{Al}_2\text{Si}_3\text{O}_{12} \]

At higher temperatures: Reactants become solid solutions, too:

\[ \text{Mg(Mg,Al)(Si,Al)}_2\text{O}_6 \rightarrow \text{(Ca,Mg)(Mg,Al)(Si,Al)}_2\text{O}_6 \rightarrow \]

opx (En + Ts) cpx (Di + Ts + cEn)

(Figure 3 of Wood and Yuen, 1983)
plagioclase $\rightarrow$ spinel $\rightarrow$ garnet

lherzolite transitions

Calculated phase relations for model lherzolite and basalt compositions in the CaO-MgO-Al$_2$O$_3$-SiO$_2$ system. See text for details.

(Figure 4 of Wood and Yuen, 1983)
plagioclase → spinel lherzolite transition

At very low temperatures:

\[
CaAl_2Si_2O_8 + 2 Mg_2SiO_4 \\
\text{plag} \quad \text{olv}
\]

\downarrow \text{ (increasing P)}

\[
MgAl_2O_4 + Mg_2Si_2O_6 + CaMgSi_2O_6 \\
\text{spinel} \quad \text{opx} \quad \text{cpx}
\]

Products are nearly pure phases. Plagioclase has relatively high entropy.

At higher temperatures: Products become solid solutions:

\[
Mg(Mg,Al)(Si,Al)_2O_6 \quad (Ca,Mg)(Mg,Al)(Si,Al)_2O_6 \\
\text{opx (En + Ts)} \quad \text{cpx (Di + Ts + cEn)}
\]
basalt → eclogite analogue transition

At low temperatures:

\[ 1.55 \text{Mg}_2\text{Si}_2\text{O}_6 + \text{CaAl}_2\text{Si}_2\text{O}_8 \]

\[ \text{opx} \quad \text{plag} \]

↓ (increasing P)

\[ 0.85 \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 0.15 \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \]

garnet solid solution (pyrope + grossular)

\[ + 0.55 \text{CaMgSi}_2\text{O}_6 + \text{SiO}_2 \]

clinopyroxene quartz

Pyroxenes are nearly pure phases, but appear as both reactants and products. Plagioclase has relatively high entropy.

ΔS<0

At higher temperatures:

Pyroxenes become solid solutions:

\[ \text{Mg(Mg,Al)(Si,Al)}_2\text{O}_6 \]  \[ \text{(Ca,Mg)(Mg,Al)(Si,Al)}_2\text{O}_6 \]

\[ \text{opx (En + Ts)} \quad \text{cpx (Di + Ts + cEn)} \]
plagioclase → spinel → garnet
lherzolite transitions

Calculated Phase Boundaries for a 6 Component
Lherzolite Containing Na and Fe(II)

Calculated phase boundaries for pyrolite composition of Table 1, excluding the effects of Cr₂O₃.

Na partitions into cpx
Fe²⁺ partitions into gt
Cr and Fe³⁺ partition into sp

(Figure 5 of Wood and Yuen, 1983)
plagioclase → spinel → garnet lherzolite transitions

Depth of the plagioclase lherzolite-spinel lherzolite transition as a function of age for pyrolite composition. Note that the age-depth function is double valued but that the transition dies out at ages > 20 Myr.

(Figure 6 of Wood and Yuen, 1983)
Plagioclase $\rightarrow$ Spinel $\rightarrow$ Garnet lherzolite transitions

Colder (older) geotherms intersect GT lherz at greater depths, so more lithosphere is (less dense) SP lherz.

Depth of the spinel lherzolite-garnet lherzolite transition as a function of age for a plate cooling conductively in the manner shown in Fig. 1b. Note the effect of increased thermal diffusivity and the differences between idealized CMAS compositions and pyrolite.
plagioclase → spinel → garnet lherzolite transitions

The greater thickness of less dense (buoyant) sp lherz in older (colder) lithosphere generates isostatic uplift.

Calculated uplift of the ocean floor relative to the $t^{1/2}$ curve due to the garnet-spinel transition. Comparison with data from Parsons and Sclater. Open circles with vertical bars: North Atlantic data with standard deviation; dash-dot curve: data from Parsons and Sclater; hatchured area denotes likely range for peridotitic mantle.

140-220 m of uplift from spinel lherz

(Figure 8 of Wood and Yuen, 1983)
Density as a function of pressure and temperature for a Hawaiian Pyrolite mantle composition.

(Figure 3a of Kaus et al., 2005)
plagioclase → spinel → garnet lherzolite transitions

Density as a function of pressure and temperature for a Hawaiian Pyrolite mantle composition.

(Figure 3a of Kaus et al., 2005)

Investigate effect on basin subsidence associated with extensional rifting.
Density as a function of pressure and temperature for a Hawaiian Pyrolite mantle composition with a bulk chemical composition given in Table 1. Superposed lines in panel (B) shows the $P-T$ distribution in a lithosphere with parameters of Fig. 5 and $\delta$=6 (see Section 4 of the text).

(Figure 3 of Kaus et al., 2005)
plagioclase → spinel → garnet lherzolite transitions

**Uplift and reduced subsidence due to less dense (buoyant) plag lherz in young (hot) rifting.**

**Enhanced subsidence due to denser gt lherz in older (colder) post-rift stage.**

Effect of phase transitions on basin subsidence for a model with \( d=3 \), \( H_{\text{crust}}^{\text{pre}}=35 \) km, \( H_{\text{mantle}}^{\text{pre}}=90 \) km and \( T_{\text{base}}=1300^\circ \text{C} \). (A) Comparison of a model with phase transitions and a model without phase transitions. The model with phase transitions has a ‘totalcrust’ crustal density and a MOR mantle density. The model without phase transitions has been computed with \( q_0^c=2900 \) kgm\(^{-3}\).

“Depending on the mineralogy, the additional post-rift subsidence ranges from ~30% to 100%.”

(Figure 4a of Kaus et al., 2005)
Results of 2-D computations with phase transitions activated in the mantle only (MOR-model). The maximum stretching factor in the center of the basin is 3. The upper crust has a $T$-dependent density with $q_0=2700$ kgm$^{-3}$ and the lower a $T$-dependent density with $q_0=2900$ kgm$^{-3}$. The initial crustal thickness is 35 km; stretching is active for 10 myr and the elastic thickness is 0 km. Plagioclase lherzolite appears in the mantle lithosphere during rifting but disappears after rifting has ceased. Modelling results have been obtained with TECMOD2D (http://www.geomodsol.com).

(Figure 8 of Kaus et al., 2005)
Results of 2-D computations with phase transitions activated in the mantle only (MOR-model). The maximum stretching factor in the center of the basin is 3. The upper crust has a $T$-dependent density with $q_0 = 2700 \text{ kgm}^{-3}$ and the lower a $T$-dependent density with $q_0 = 2900 \text{ kgm}^{-3}$. The initial crustal thickness is 35 km; stretching is active for 10 myr and the elastic thickness is 0 km. Plagioclase lherzolite appears in the mantle lithosphere during rifting but disappears after rifting has ceased. Modelling results have been obtained with TECMOD2D (http://www.geomodsol.com).

(Figure 8 of Kaus et al., 2005)
Results of 2-D computations with phase transitions activated in the mantle only (MOR-model). The maximum stretching factor in the center of the basin is 3. The upper crust has a $T$-dependent density with $q_0=2700$ kgm$^{-3}$ and the lower a $T$-dependent density with $q_0=2900$ kgm$^{-3}$. The initial crustal thickness is 35 km; stretching is active for 10 myr and the elastic thickness is 0 km. Plagioclase lherzolite appears in the mantle lithosphere during rifting but disappears after rifting has ceased. Modelling results have been obtained with TECMOD2D (http://www.geomodsol.com).

(Figure 8 of Kaus et al., 2005)
A Useful Rule: “Garnet Eats Everything”

\[ \mu_i = \mu_i^0 + nRT \ln a_i \]

\[ a_i \leq 1 \rightarrow RT \ln a_i \leq 0 \]

Dilute solutions have lower chemical potentials (free energies) than pure end-members.

Complex solutions have expanded stability fields.

\[ (Ca,Mg,Fe^{2+})_3^{\text{VIII}}[(Al,Fe^{3+})_2,(Mg,Fe^{2+})Si]^{\text{VI}}Si_3^{\text{IV}}O_{12} \]

(a simple Ca-Mg-Fe garnet-majorite solid solution)

Thus, phase transitions involving garnet tend to be very broad.
eclogite → garnetite transition

\[ \text{Mg}_3(\text{Al}_2,\text{MgSi})\text{Si}_3\text{O}_{12} \]

\[ \text{garnet-majourite solid solution} \]

\[ \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} \]

garnet

\[ \text{garnet-majorite solid solution} \]

\[ \text{Mg}(\text{Mg,Al})(\text{Si,Al})_2\text{O}_6 \]

pyroxene

[A] Isothermal pressure-composition diagram showing experimental data of Akaogi and Akimoto (1977) and pyroxene-garnet miscibility gap fit to initial (RAW) and adjusted (ADJ.) data base.

(Figure 1a of Bina and Wood, 1984)
garnet → silicate perovskite transition

Transition sequence of majorite garnet in pyrolite mantle at 1600°C as a function of pressure. Dotted lines indicate approximate compositions of garnet and perovskite in the transition zone and lower mantle, respectively (see Section 3.4). Dashed lines show pressure interval of about 2.7 GPa for the transition from majorite garnet to aluminous perovskite.

Abbreviations: Pv, perovskite; Co, corundum; Ga, garnet; Il, ilmenite; Sp, spinel; St, stishovite.

(Figure 12 of Kubo and Akaogi, 2000)
Two Phase Transitions Can Interact by Cation Exchange

Example 1: the olivine $\alpha \rightarrow \beta$ transition and the cpx$\rightarrow$gt transition

$$\alpha-(Mg,Fe)_2SiO_4 \rightarrow \beta-(Mg,Fe)_2SiO_4$$

$$Mg^{2+} \uparrow \downarrow Fe^{2+}$$

cpx-$(Ca,Mg,Fe)(Mg,Fe,Al)(Si,Al)_2O_6 \rightarrow gt-(Ca,Mg,Fe)_3([Al_2,(MgSi,FeSi)]Si_3O_{12})$
Mg-Fe exchange between olivine and garnet:

\[
\begin{align*}
\alpha & \quad \text{Fe}^{2+} \\
& \quad \text{Mg}^{2+} \\
& \quad \text{gt}
\end{align*}
\]

**Mg-enriched olivine sharpens** $\alpha \rightarrow \beta$ transition

Equilibrium mineral proportions and compositions as functions of mantle depth, for $(\text{Mg}_{0.89}\text{Fe}_{0.11})_2\text{SiO}_4$ olivine in isolation (Fo89) and for a model (pyrolite) mantle composition. Mineral proportions are as volume fraction, shown by bold white lines; compositions are in terms of $\text{Mg}/[\text{Mg+Fe}]$, and are shown by colours and by dotted contours at 1% intervals. With increasing depth, olivine ($\alpha$) transforms to wadsleyite ($\beta$) near 410 km, and orthopyroxene (opx) gradually dissolves into clinopyroxene (cpx) which in turn dissolves into garnet (gt). In the pyrolite mantle composition, all phases grow more Mg-rich with increasing depth. (Figure based on data from Irifune and Isshiki.)

(Figure 1 of Bina, 1998; after Irifune and Isshiki, 1998)
Two Phase Transitions Can Interact by Cation Exchange

Example 1: the olivine $\alpha \rightarrow \beta$ transition and the cpx$\rightarrow$gt transition

\[
\alpha-(Mg,Fe)_2SiO_4 \rightarrow \beta-(Mg,Fe)_2SiO_4
\]

\[
\text{Mg}^{2+} \uparrow \downarrow \text{Fe}^{2+}
\]

\[
cpx-(Ca,Mg,Fe)(Mg,Fe,Al)(Si,Al)_2O_6 \rightarrow gt-(Ca,Mg,Fe)_3([Al_2,(MgSi,FeSi)]Si_3O_{12})
\]

Example 2: the olivine $\gamma \rightarrow pv+mw$ transition and the gt$\rightarrow$pv transition

\[
\gamma-(Mg,Fe)_2SiO_4 \rightarrow pv-(Mg,Fe)SiO_3 + mw-(Mg,Fe)O
\]

\[
\text{Mg}^{2+} \uparrow \downarrow \text{Fe}^{2+}, \text{Fe}^{3+}
\]

\[
gt-(Mg,Fe)_3([(Al,Fe^{3+})_2,(MgSi,FeSi)]Si_3O_{12}) \rightarrow pv-(Mg,Fe^{2+},Fe^{3+},Al)SiO_3
\]
ringwoodite ($\gamma$) plus garnet $\rightarrow$ silicate perovskite plus magnesiowüstite (ferropericlase) transition

The first appearance of pv arises from the $\gamma \rightarrow$ pv + mw transition (sharp). More pv from the gt $\rightarrow$ pv transition (broad) is formed later.

Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.

(after Figure 4 of Wood, 2000)
ringwoodite (γ) plus garnet → silicate perovskite plus magnesiowüstite (ferropericlase) transition

The first appearance of pv arises from the γ → pv + mw transition (sharp). More pv from the gt → pv transition (broad) is formed later.

Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.
ringwoodite (γ) plus garnet → silicate perovskite plus magnesiowüstite (ferropericlaselace) transition

The first appearance of pv arises from the γ → pv + mw transition (sharp). More pv from the gt → pv transition (broad) is formed later.

Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.

(after Figure 4 of Wood, 2000)
ringwoodite ($\gamma$) plus garnet $\rightarrow$ silicate perovskite plus magnesiowüstite (ferropericlase) transition

The first appearance of $pv$ arises from the $\gamma \rightarrow pv + mw$ transition (sharp). More $pv$ from the $gt \rightarrow pv$ transition (broad) is formed later.

Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.
ringwoodite ($\gamma$) plus garnet $\rightarrow$ silicate perovskite plus magnesiowüstite (ferropericlase) transition

The first appearance of pv arises from the $\gamma \rightarrow$ pv + mw transition (sharp). More pv from the gt $\rightarrow$ pv transition (broad) is formed later.

Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.
Volumic proportions of minerals and phases present in the pyrolite composition as a function of depth, along the 1000 K (top) and 1500 K (middle) and 1600 K (bottom) adiabats. Dashed lines give the proportions of ‘virtual phases’, which are part of the garnet solid solution. en: enstatite; di: diopside; jd: jadeite; Ca-gt: Ca-garnet; Na-maj: Na-majorite; other symbols are defined in Fig. 1 and Fig. 2.

The $\text{gt} \rightarrow \text{pv}$ transition is broad and does not achieve completion until after the sharp $\gamma \rightarrow \text{pv} + \text{mw}$ transition.

(Figure 3 of Vacher et al., 1998)
Phase Changes in (Mg,Fe)$_2$SiO$_4$ Olivine

Forsterite \((\alpha)\) \(\rightarrow\) Wadsleyite \((\beta)\) \(\rightarrow\) Ringwoodite \((\gamma)\)

\((Mg,Fe)SiO_3\)

Silicate Perovskite \((pv)\)

\((Mg,Fe)O\)

Magnesiowüstite \((mw)\)

(mineral structures by D. Sherman)
Equilibrium Olivine Phase Relations

\[ \gamma \rightarrow \gamma + pv + mw \rightarrow pv + mw \]

\[ \alpha \rightarrow \alpha + \beta \rightarrow \beta \]

660 km discontinuity -------->

410 km discontinuity -------->

\[ \gamma + pv + mw \]

\[ \beta + \gamma \]

\[ \alpha + \beta \]

\[ \alpha \rightarrow \alpha + \beta \rightarrow \beta \]

mantle \((\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4\) -------->

(Figure 16 from Presnall [1995])

(C.Bina, 9/2011)
Equilibrium Olivine $\alpha$-$\beta$-$\gamma$ Polymorph Phase Relations

- Univariant: $\alpha + \beta \rightarrow \alpha + \gamma$
- Divariant: $\alpha + \beta \rightarrow \beta$
- Divariant: $\alpha \rightarrow \alpha + \gamma$

Diagram showing the phase transitions and compositions under varying temperatures (hot to cold) and pressures. The diagram is based on data from Heffrich & Bina (1994).
(Mg$_{0.9}$Fe$_{0.1}$)$_2$SiO$_4$ Equilibrium Phase Assemblages

Figure from Bina, 2002
410-km seismic discontinuity uplifted in subduction zones

\[(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4: \alpha \rightarrow \alpha + \beta \rightarrow \beta\]

(Figure from Bina, 2002)
(Mg_{0.9}Fe_{0.1})_2SiO_4 Equilibria

(Figure 3 of Bina [2003])
Acoustic Velocity Gradients

(Figure from Bina, 2002)
Seismic Reflectivity

(Figure from Bina, 2002)