

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

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*Katedra geofyziky
Matematicko-fyzikální fakulta
Univerzita Karlova v Praze*

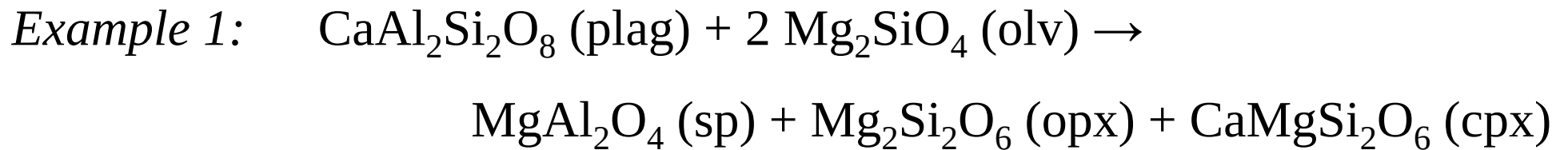
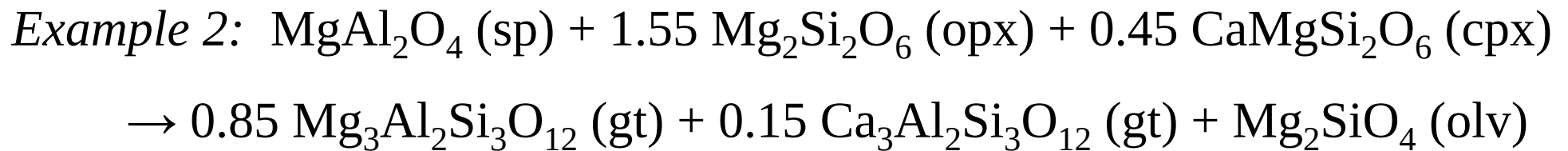
*přednášky na podzim 2011
4. lekce 2.11.*

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

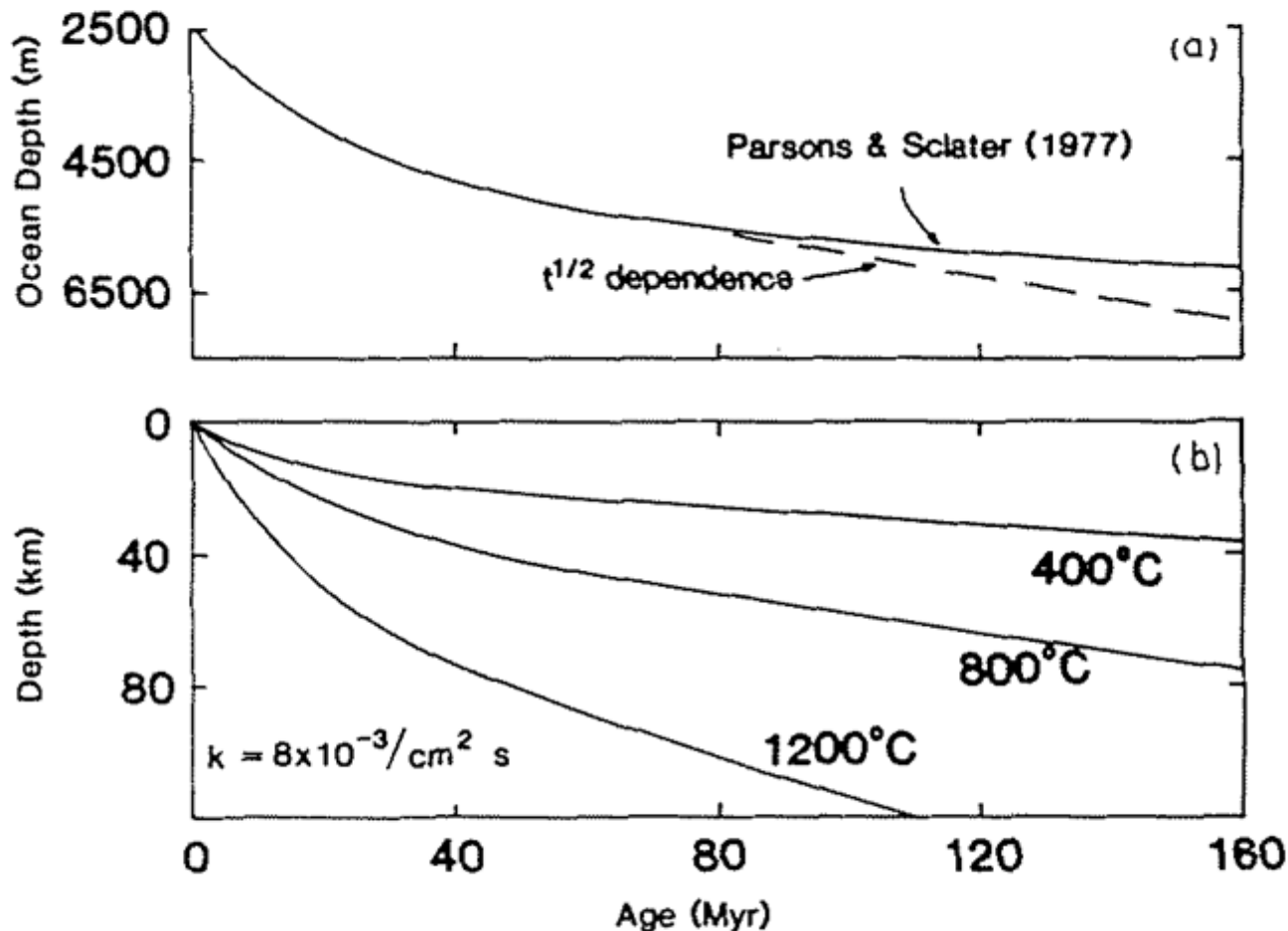
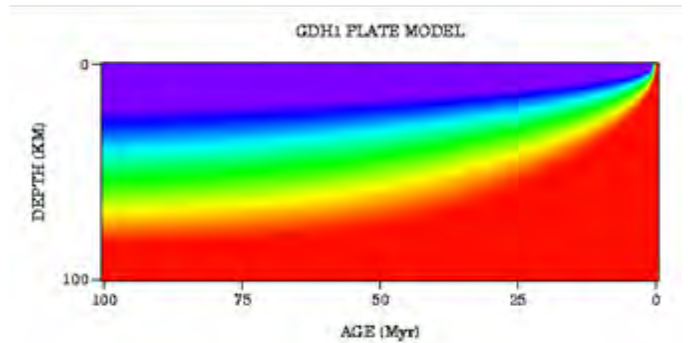


Summary 1: sp, opx and cpx increase; plag vanishes; olv decreases

Summary 2: gt and olv increase; sp vanishes; opx and cpx decrease

plagioclase → spinel → garnet
lherzolite transitions

Ocean Depth and Lithosphere Temperature–Age Relations

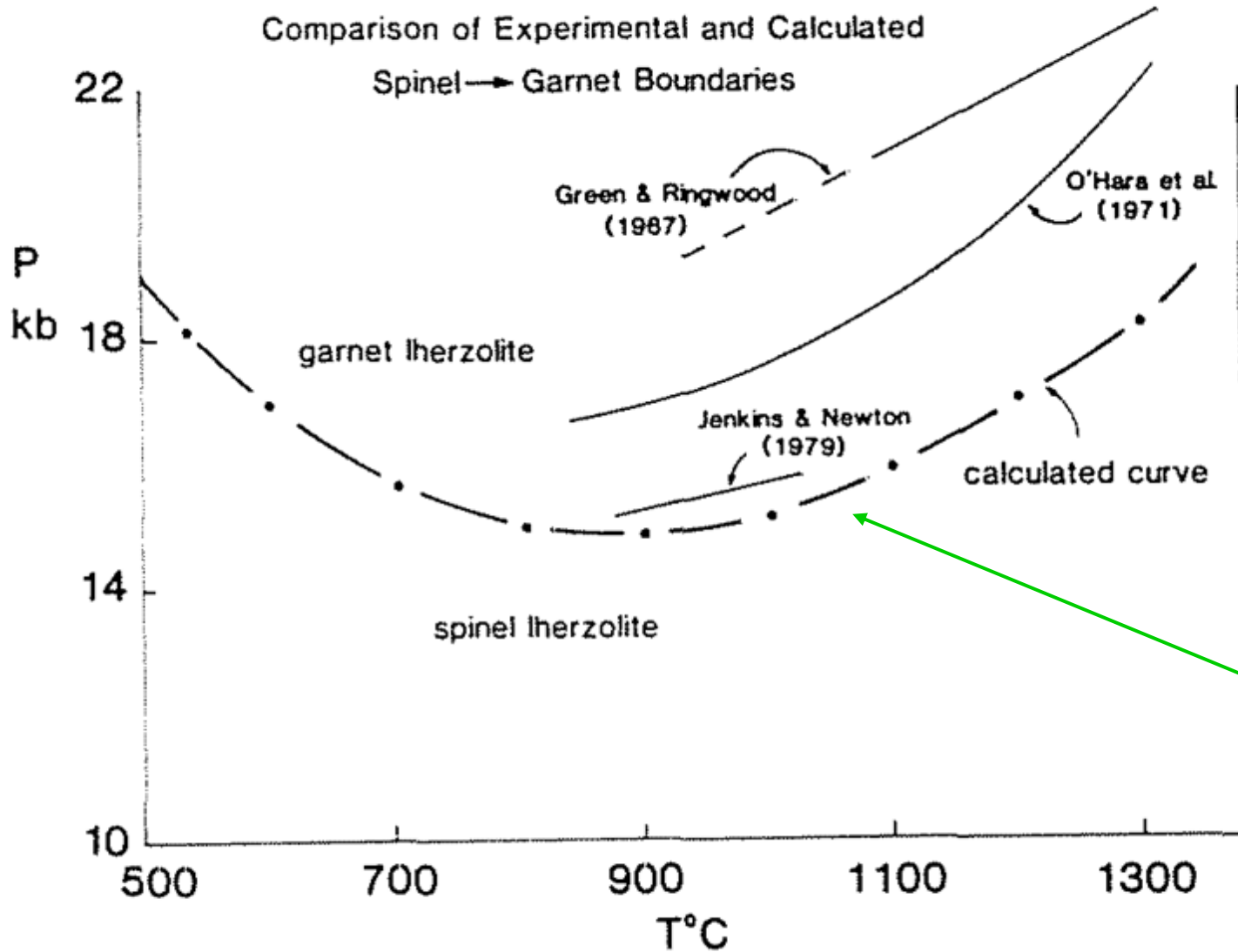


(after Stein and Stein, 1992)

(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 $8 \times 10^{-3} \text{ cm}^2/\text{s}$ and maximum temperature of 1350°C .

(Figure 1 of Wood and Yuen, 1983)

spinel → garnet lherzolite transition



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*

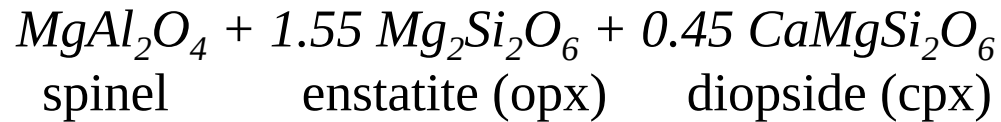
(Figure 3 of Wood and Yuen, 1983)

spinel → garnet lherzolite transition

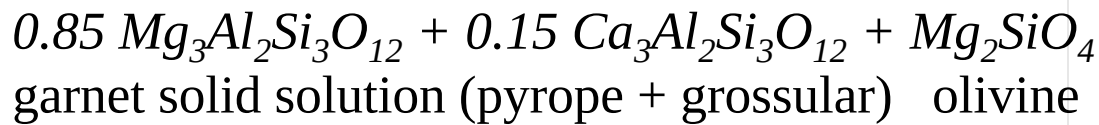
Increasing pressure:

$$\Delta V < 0$$

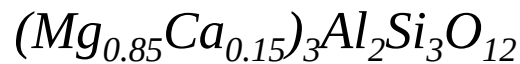
At very low temperatures:



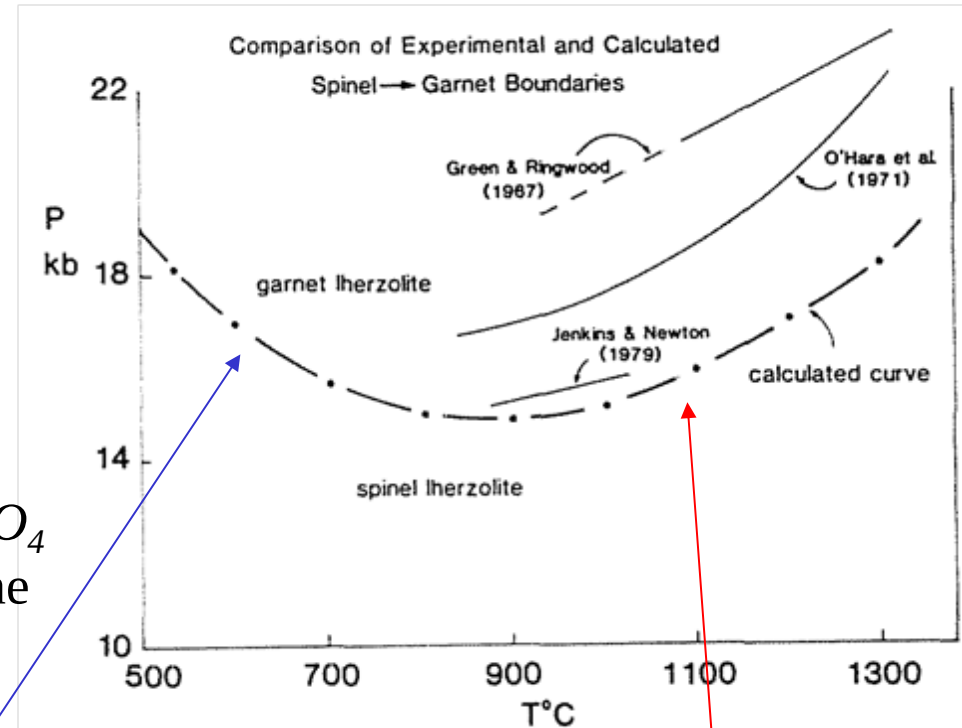
↓ (increasing P)



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

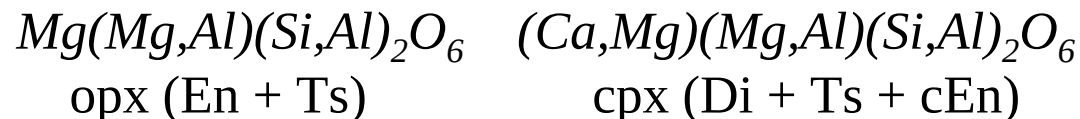


$$\Delta S > 0$$



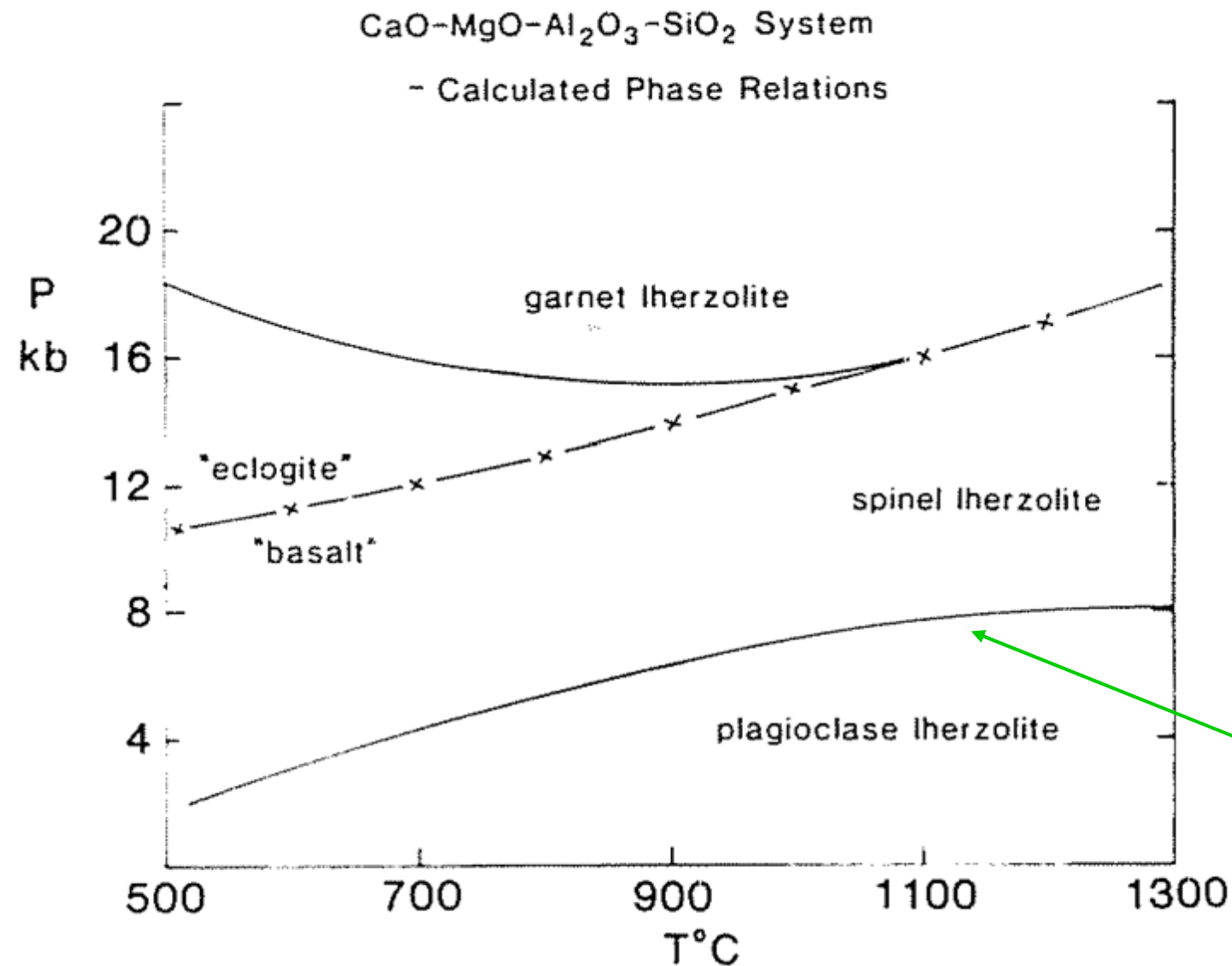
(Figure 3 of Wood and Yuen, 1983)

At higher temperatures: Reactants become solid solutions, too:



$$\Delta S < 0$$

plagioclase → spinel → garnet
herzolite transitions



Calculated phase relations for model herzolite and basalt compositions in the CaO-MgO-Al₂O₃-SiO₂ system. See text for details.

*plagioclase → spinel
herzolite transition*

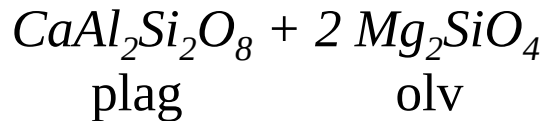
(Figure 4 of Wood and Yuen, 1983)

plagioclase → spinel lherzolite transition

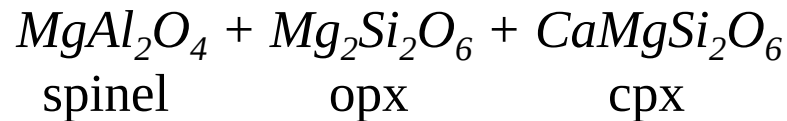
Increasing pressure:

$$\Delta V < 0$$

At very low temperatures:



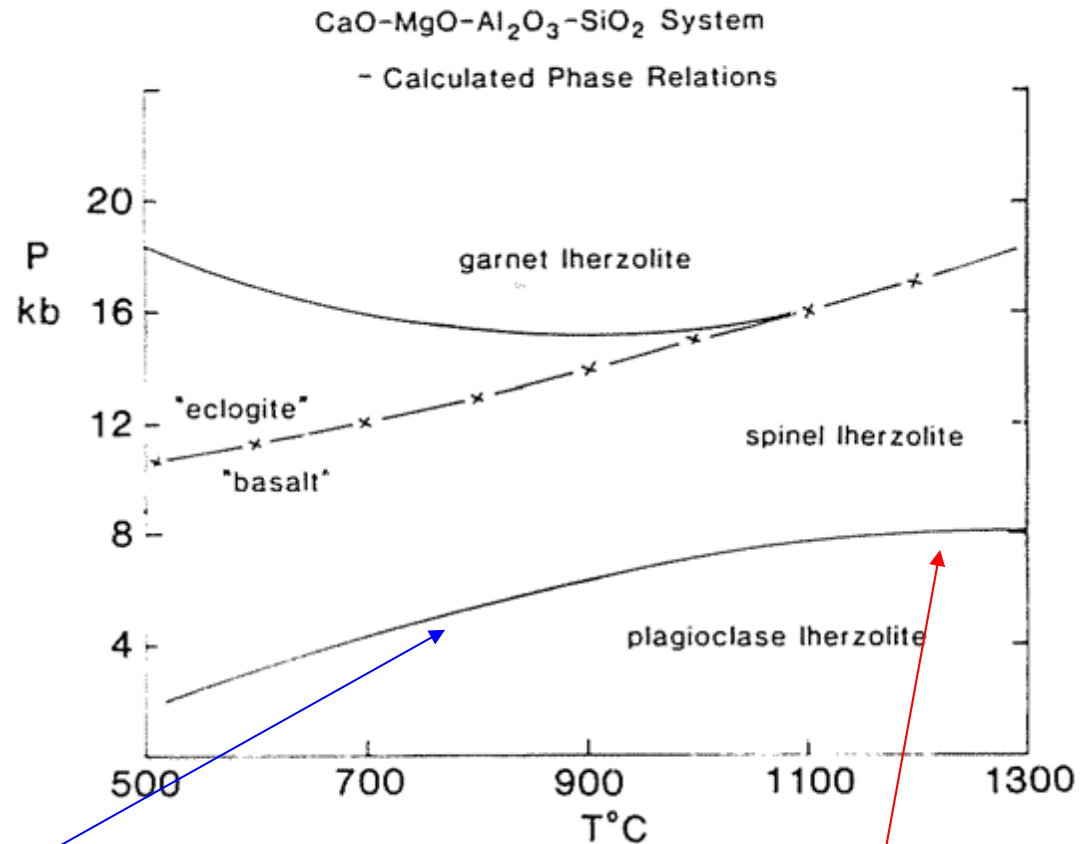
↓ (increasing P)



Products are nearly pure phases.

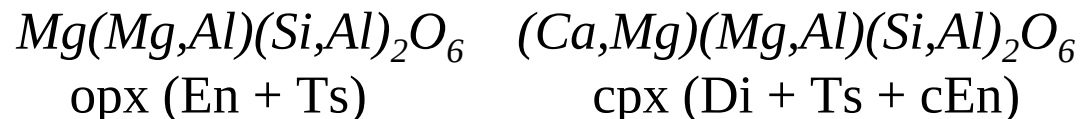
Plagioclase has relatively high entropy.

$$\Delta S < 0$$



(Figure 4 of Wood and Yuen, 1983)

At higher temperatures: Products become solid solutions:



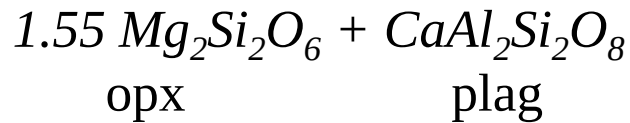
$$\Delta S > 0$$

basalt → eclogite analogue transition

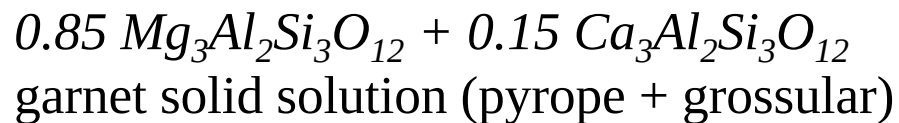
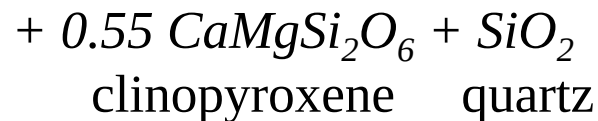
Increasing pressure:

$$\Delta V < 0$$

At low temperatures:

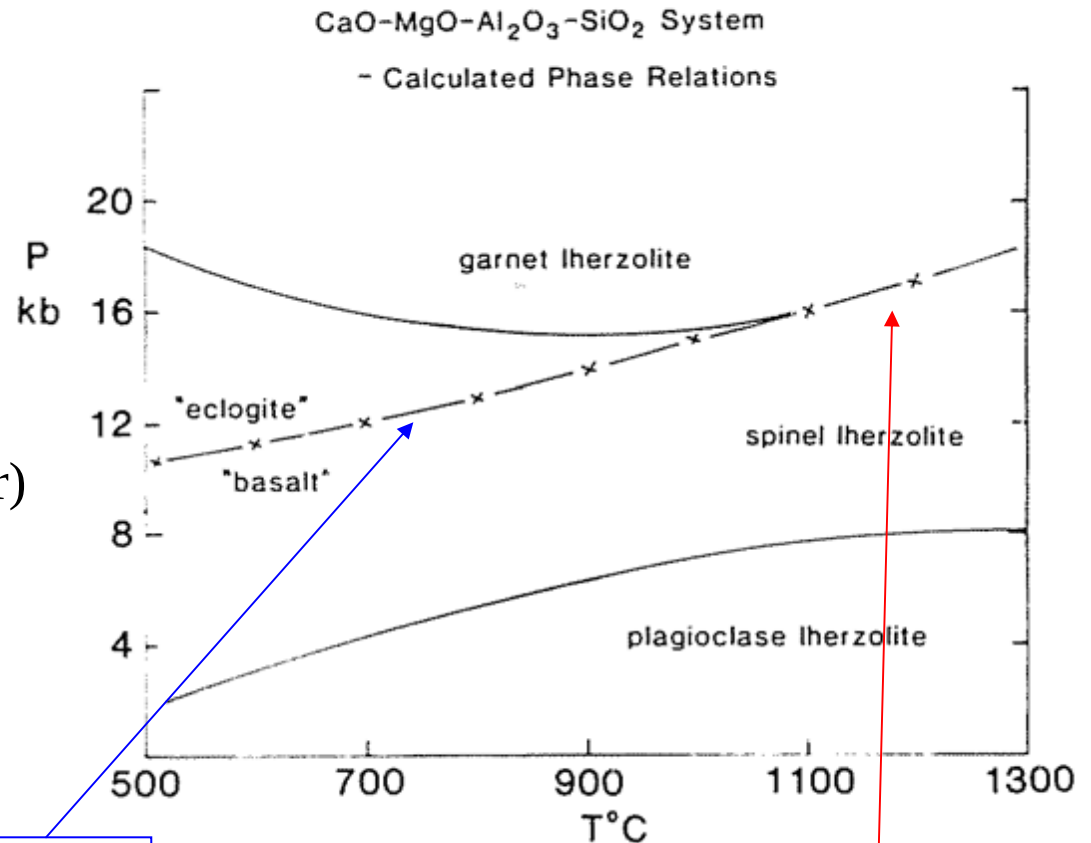


↓ (increasing P)



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

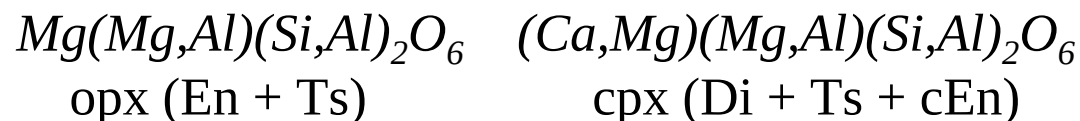
$$\Delta S < 0$$



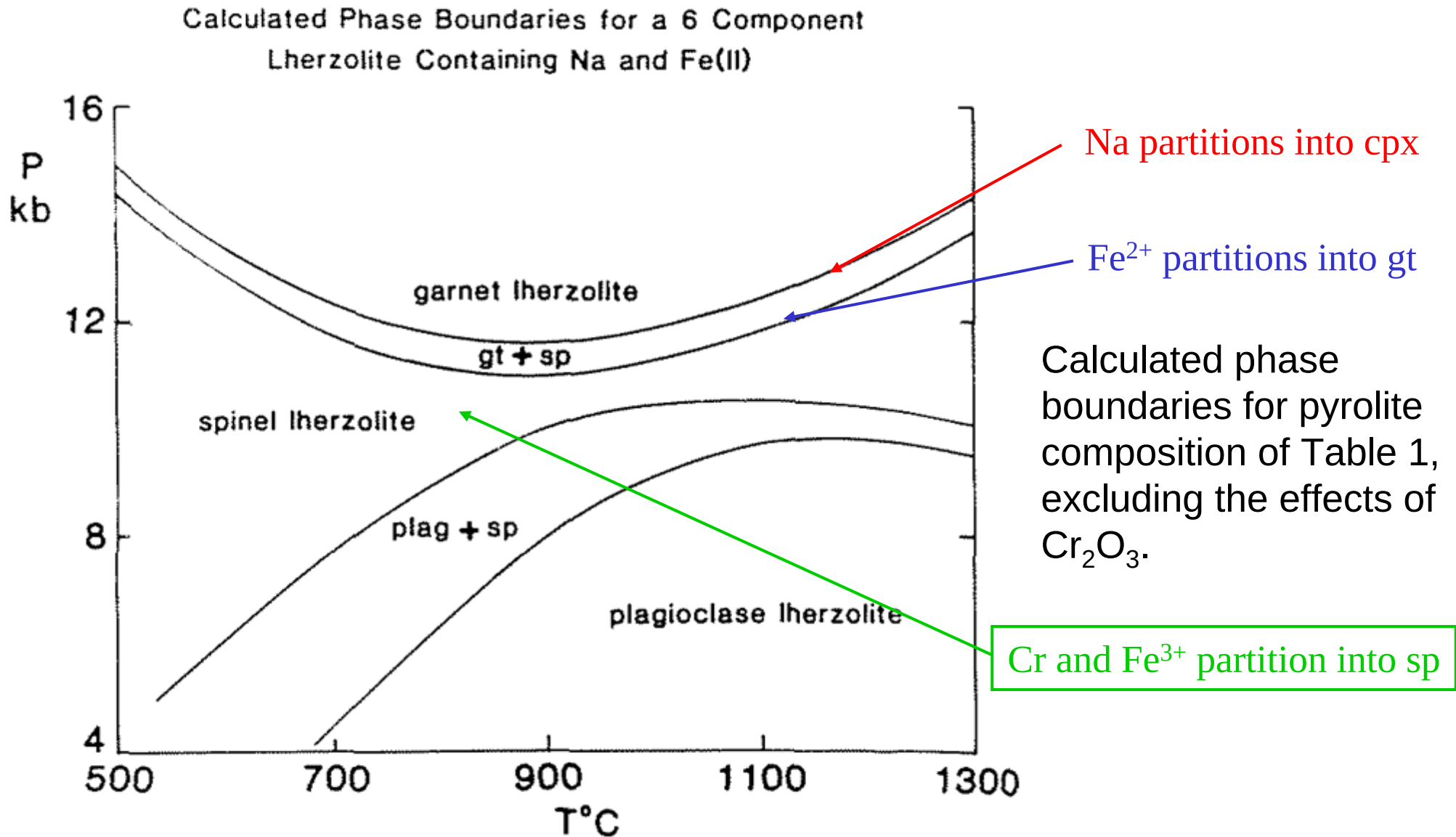
(Figure 4 of Wood and Yuen, 1983)

change in slope, not in sign

At higher temperatures: Pyroxenes become solid solutions:

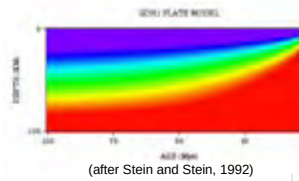
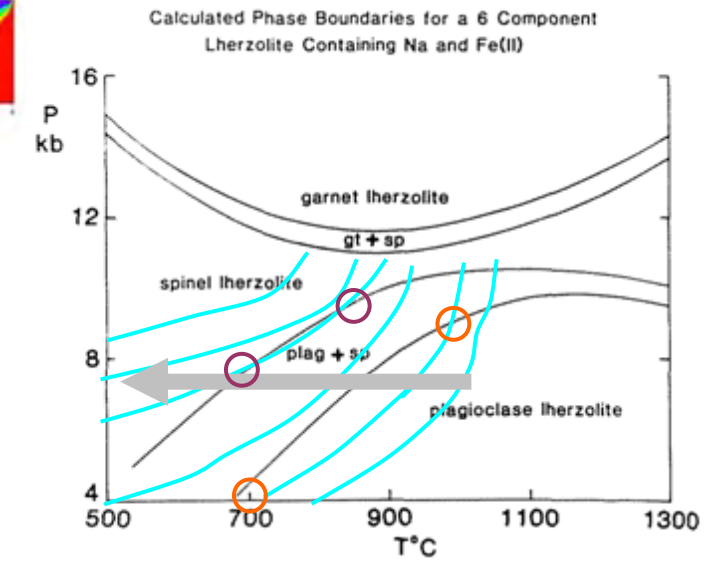


plagioclase → spinel → garnet
lherzolite transitions

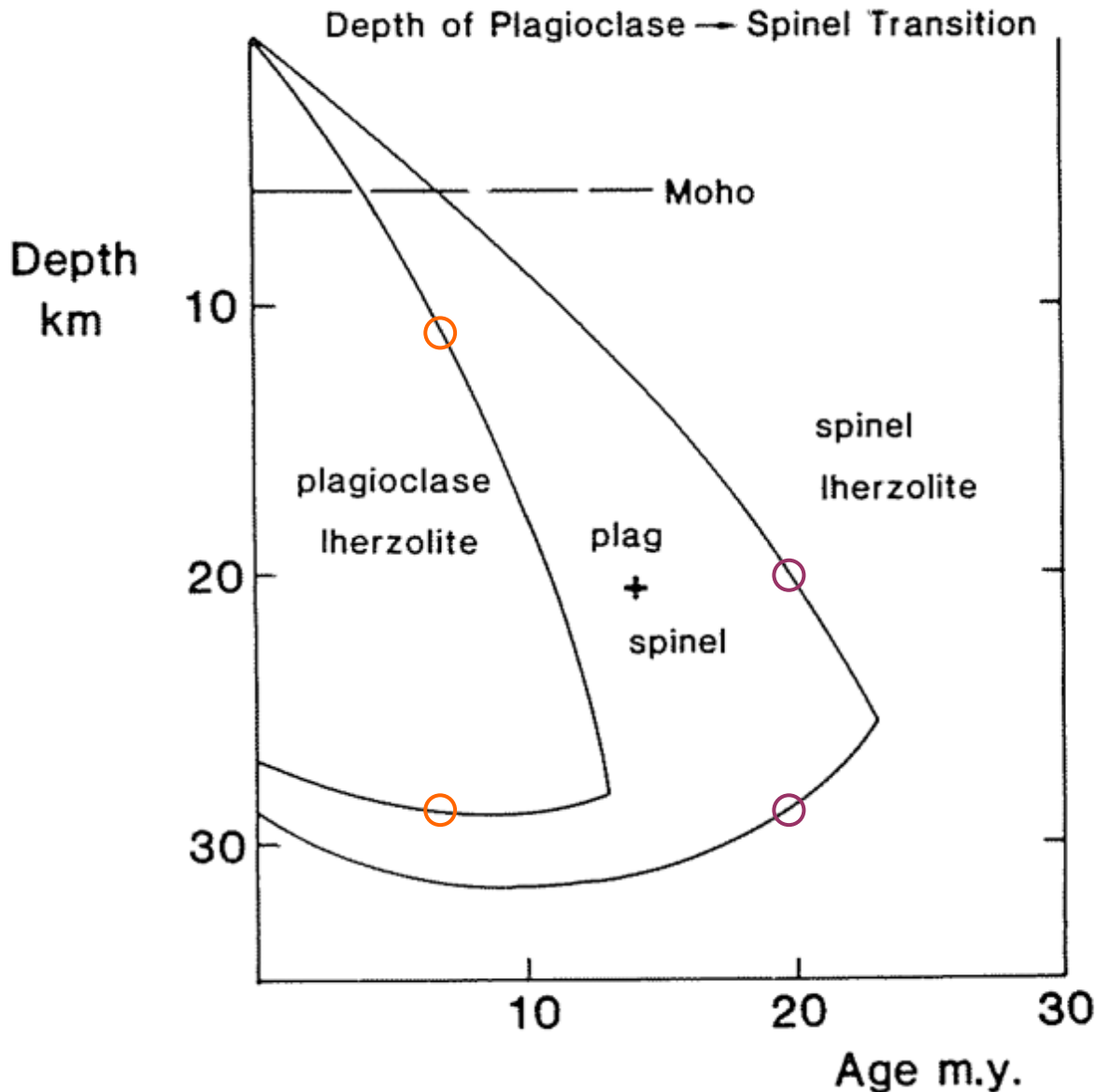


(Figure 5 of Wood and Yuen, 1983)

plagioclase → spinel → garnet
lherzolite transitions



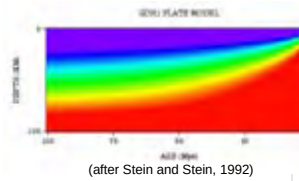
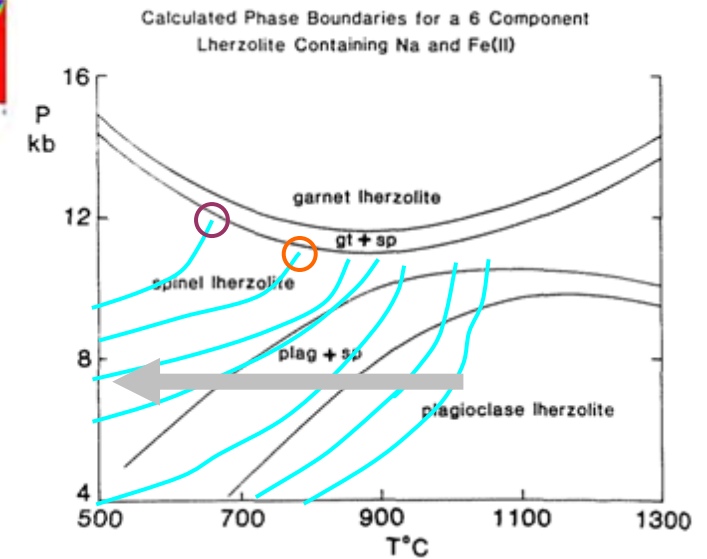
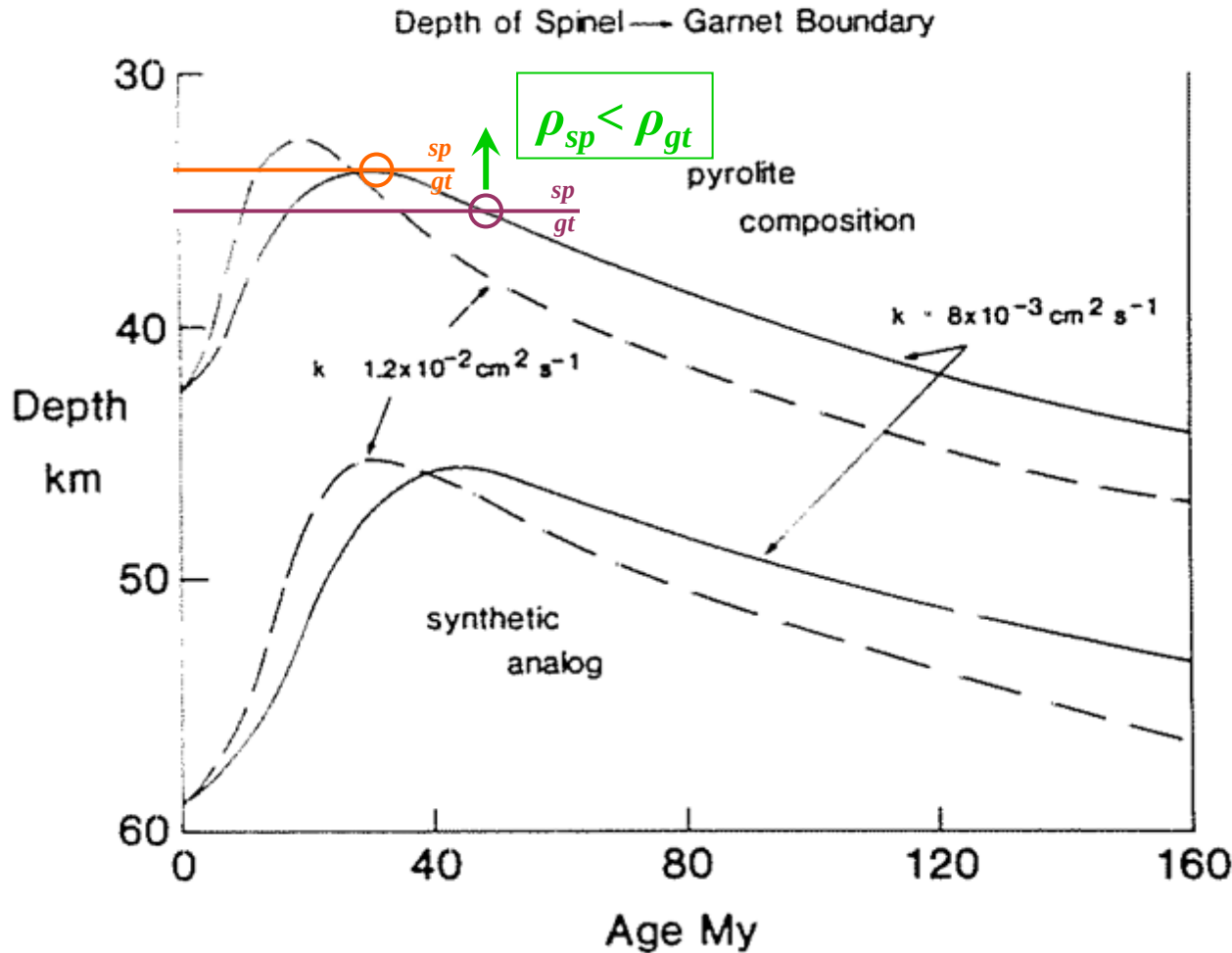
Warm (young) geotherms may intersect plag lherz field twice.



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 → spinel → garnet
lherzolite transitions



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

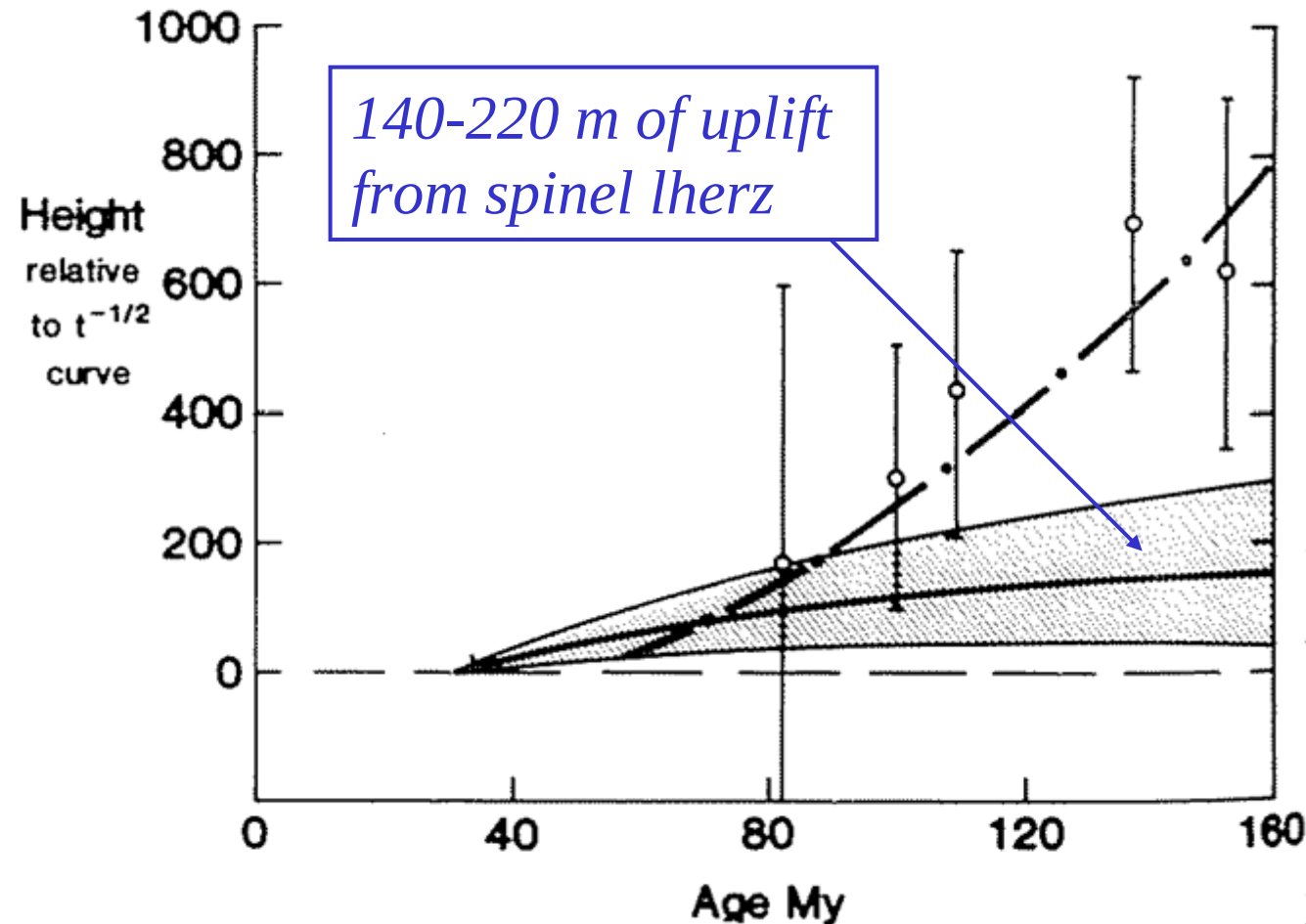
Depth of the spinel lherzolite-garnet lherzolite transition as a function of age for a plate cooling conductively in the manner shown in Fig. 1b. Note the effect of increased thermal diffusivity and the differences between idealized CMAS compositions and pyrolite.

(Figure 7 of Wood and Yuen, 1983)

plagioclase → spinel → garnet
lherzolite transitions

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

Comparison of Relative Uplift with Parsons-Sclater Data

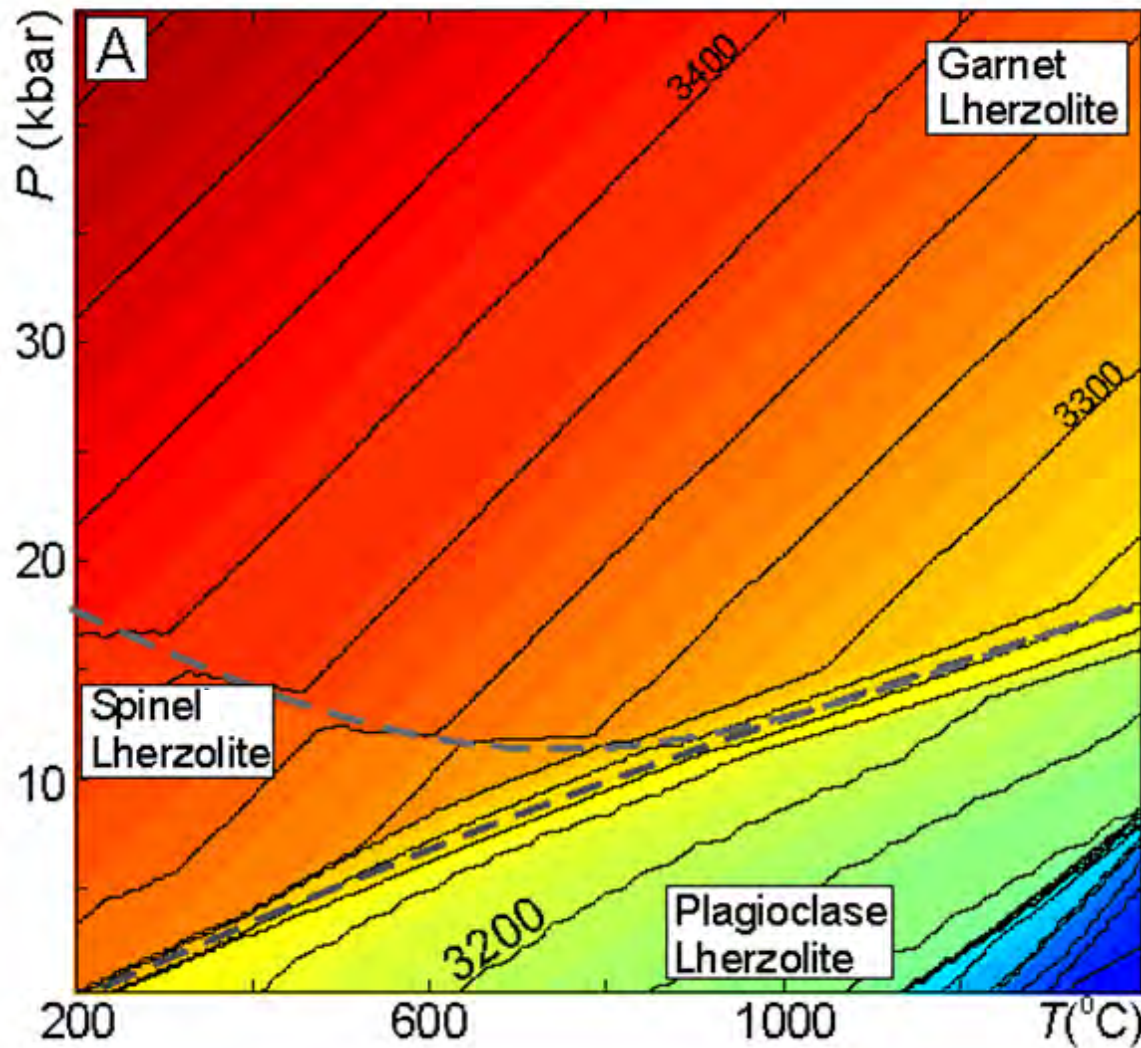


↑ $\rho_{sp} < \rho_{gt}$

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; hatched area denotes likely range for peridotitic mantle.

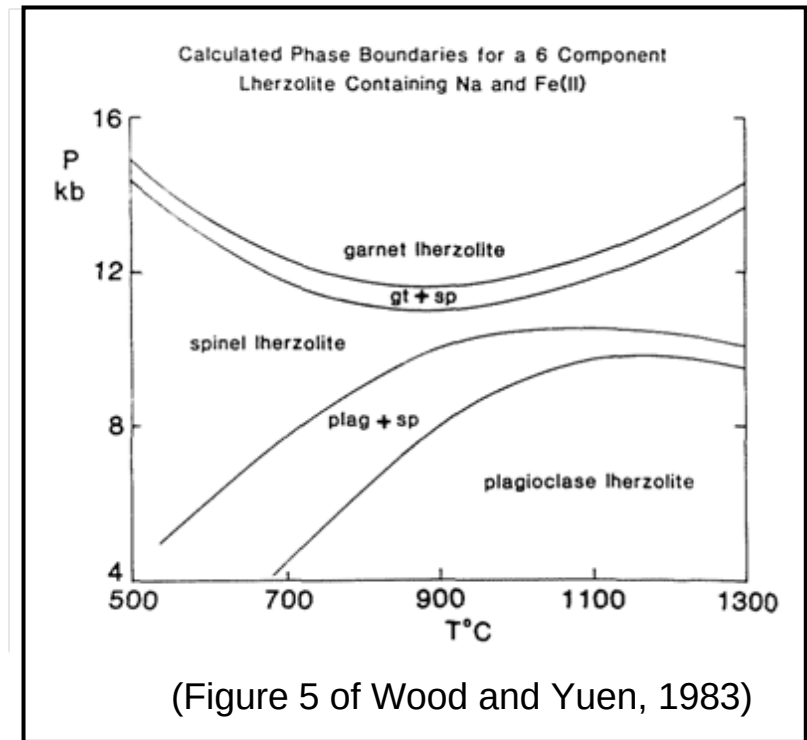
(Figure 8 of Wood and Yuen, 1983)

plagioclase → spinel → garnet
lherzolite transitions



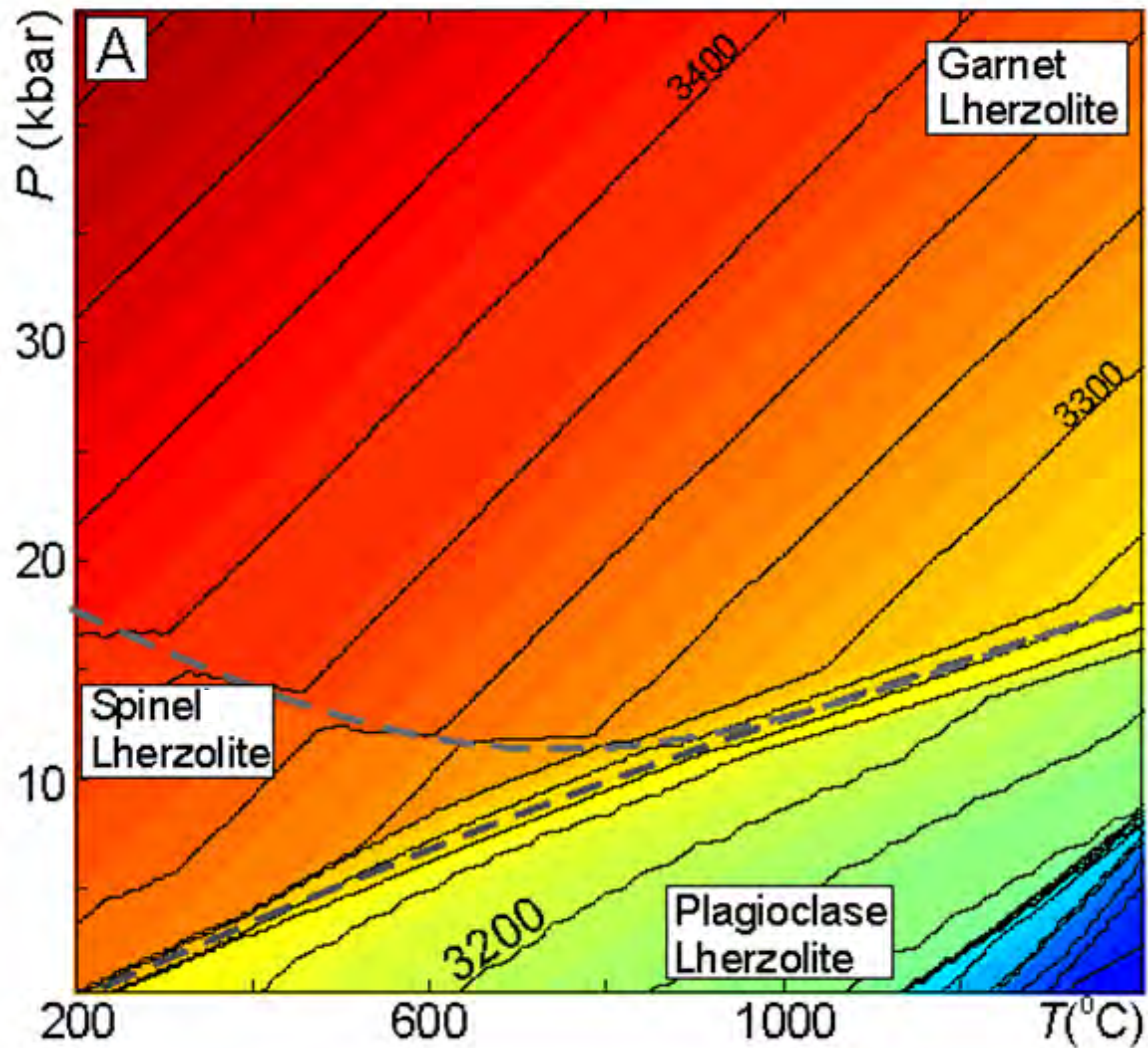
Density as a function of pressure and temperature
for a Hawaiian Pyrolite mantle composition.

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



(Figure 5 of Wood and Yuen, 1983)

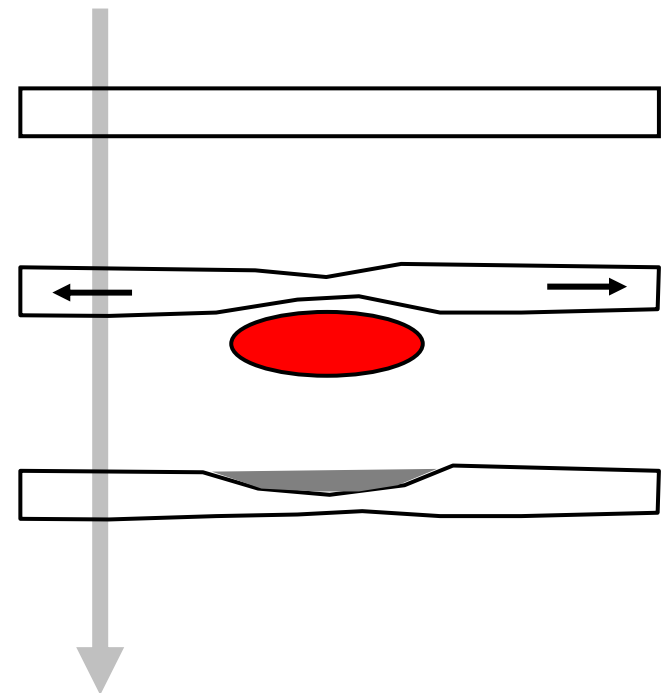
plagioclase → spinel → garnet
lherzolite transitions



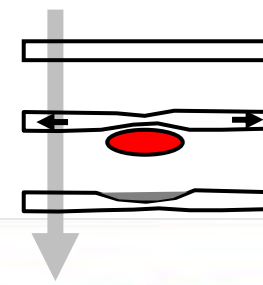
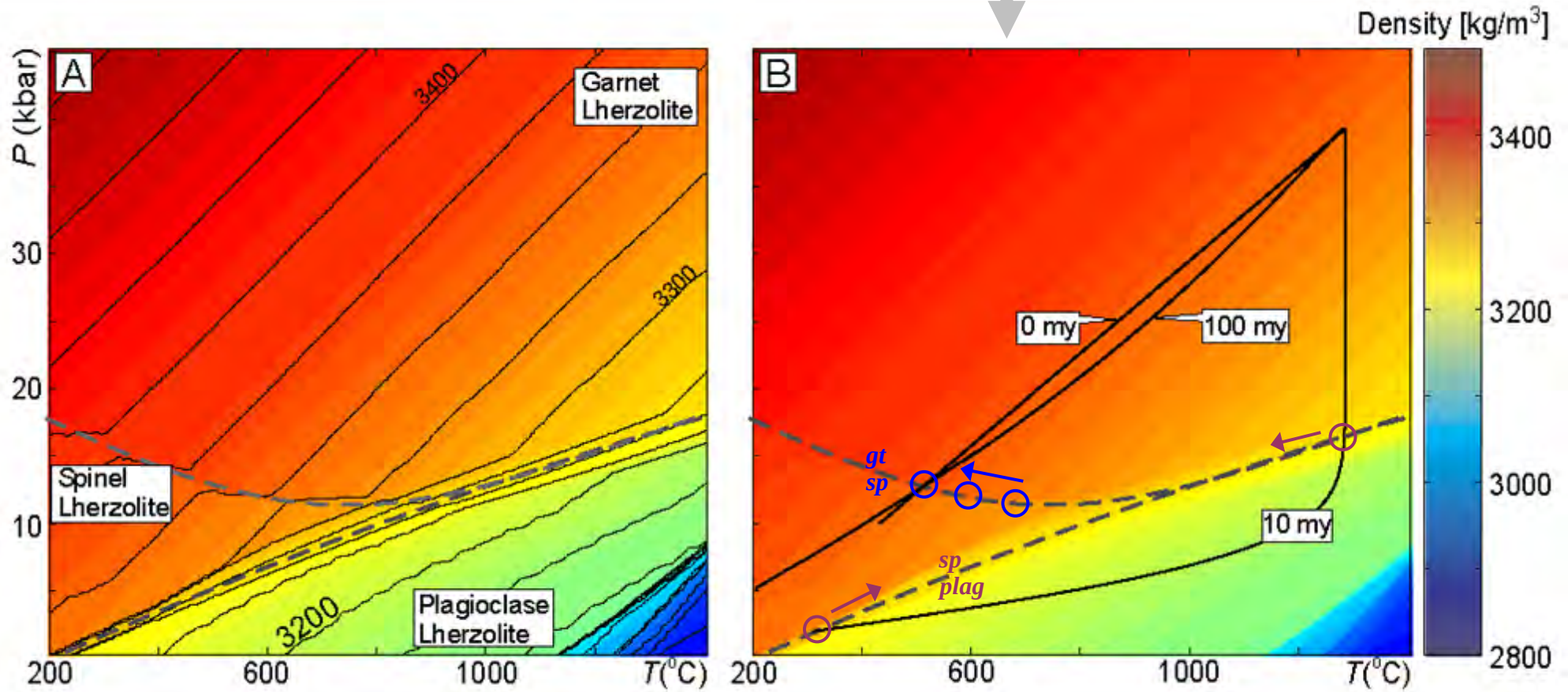
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(Figure 3a of Kaus et al., 2005)

*Investigate effect on basin
subsidence associated with
extensional rifting.*



plagioclase → spinel → garnet
herzolite transitions

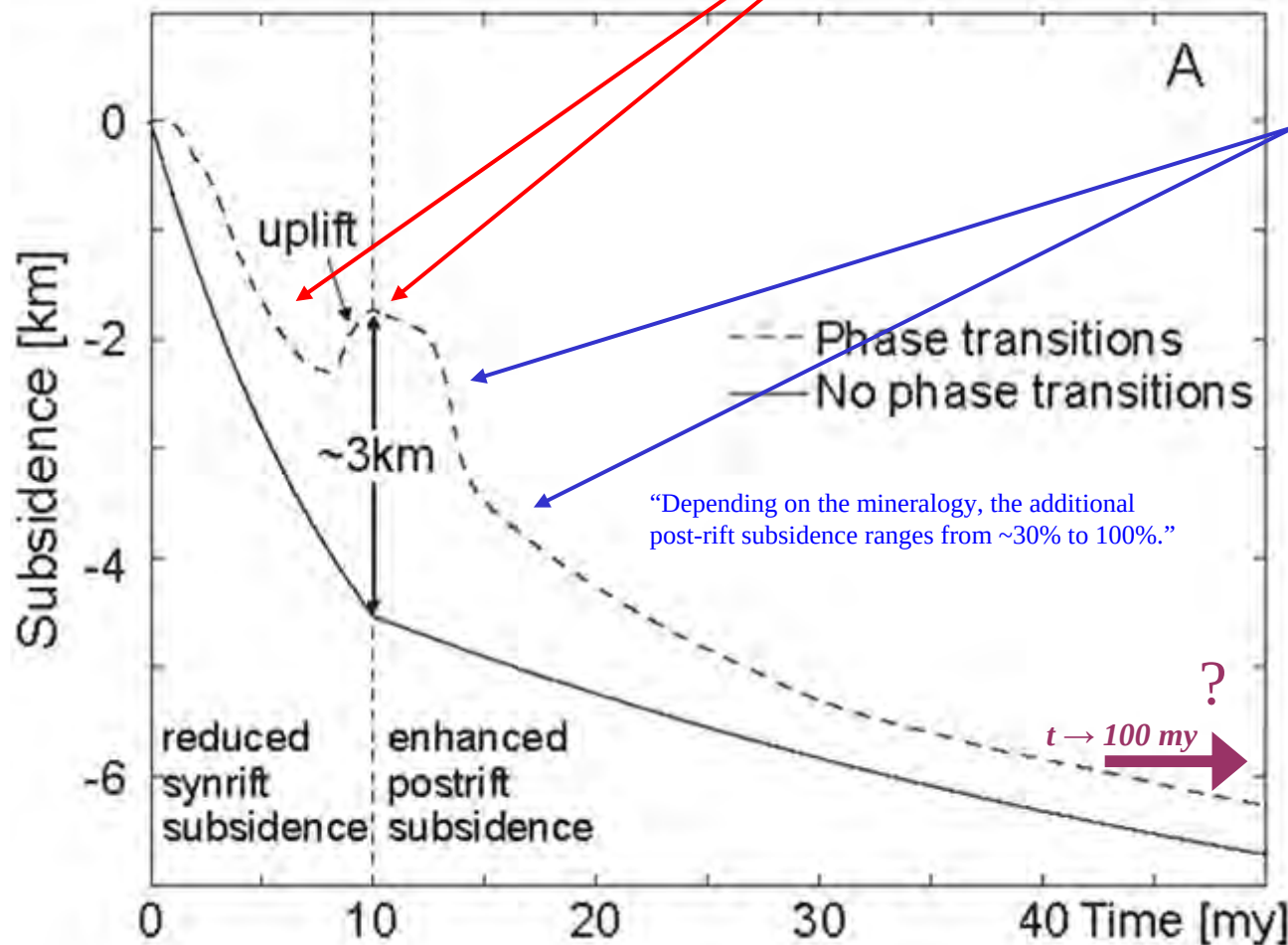


Density as a function of pressure and temperature for a Hawaiian Pyrolite mantle composition with a bulk chemical composition given in Table 1. Superposed lines in panel (B) shows the P – T distribution in a lithosphere with parameters of Fig. 5 and $\delta=6$ (see Section 4 of the text).

(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.*

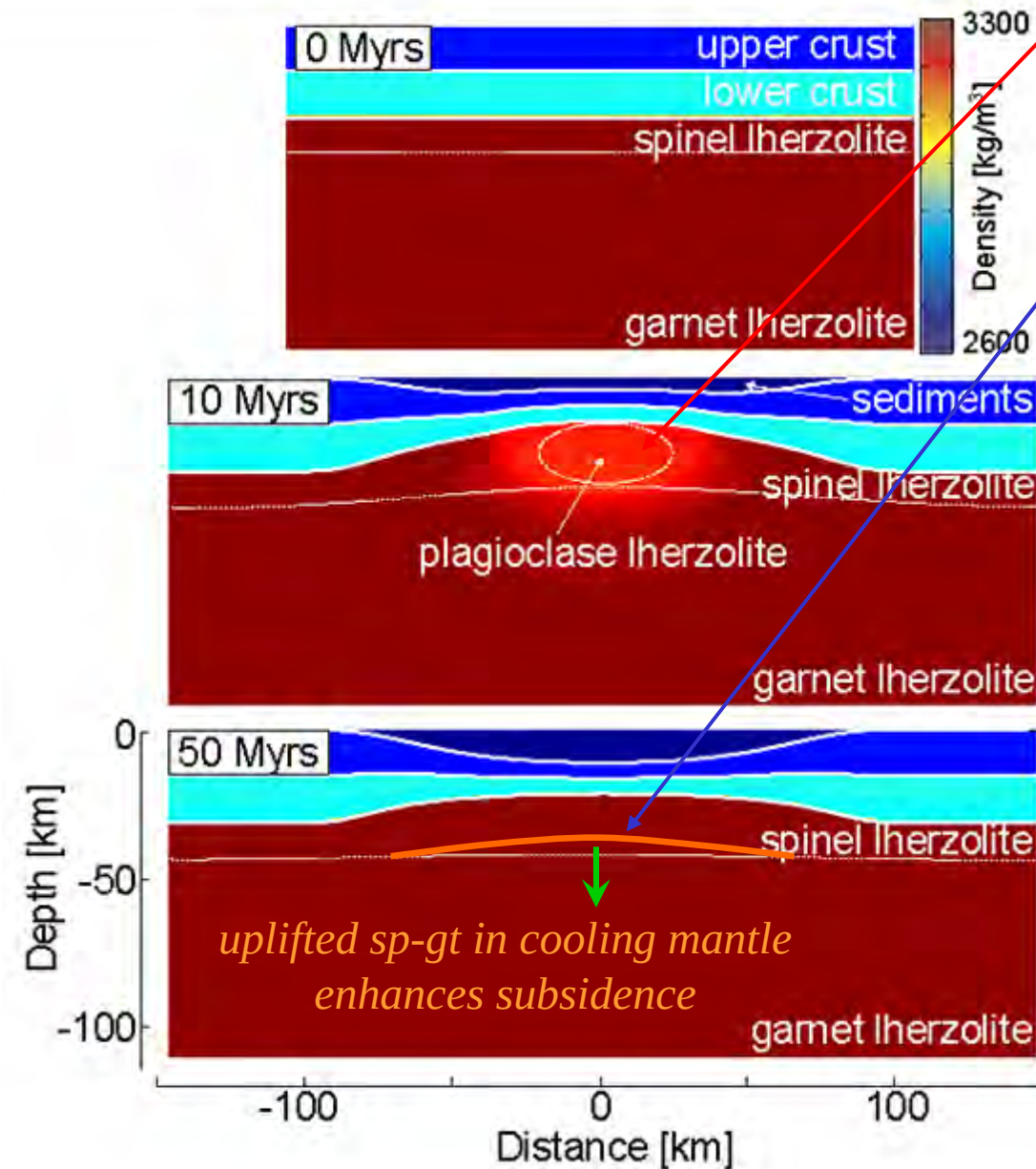
Effect of phase transitions on basin subsidence for a model with $d=3$, $H_{\text{crust}}^{\text{pre}} = 35 \text{ km}$, $H_{\text{mantle}}^{\text{pre}} = 90 \text{ km}$ and $T_{\text{base}} = 1300^\circ\text{C}$. (A) Comparison of a model with phase transitions and a model without phase transitions.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

(Figure 4a of Kaus et al., 2005)

plagioclase → spinel → garnet
herzolite transitions

Warm (rifting) geotherms intersect the plag lherz field (→uplift).

Cold (post-rifting) geotherms do not intersect the plag lherz field (→subsidence).



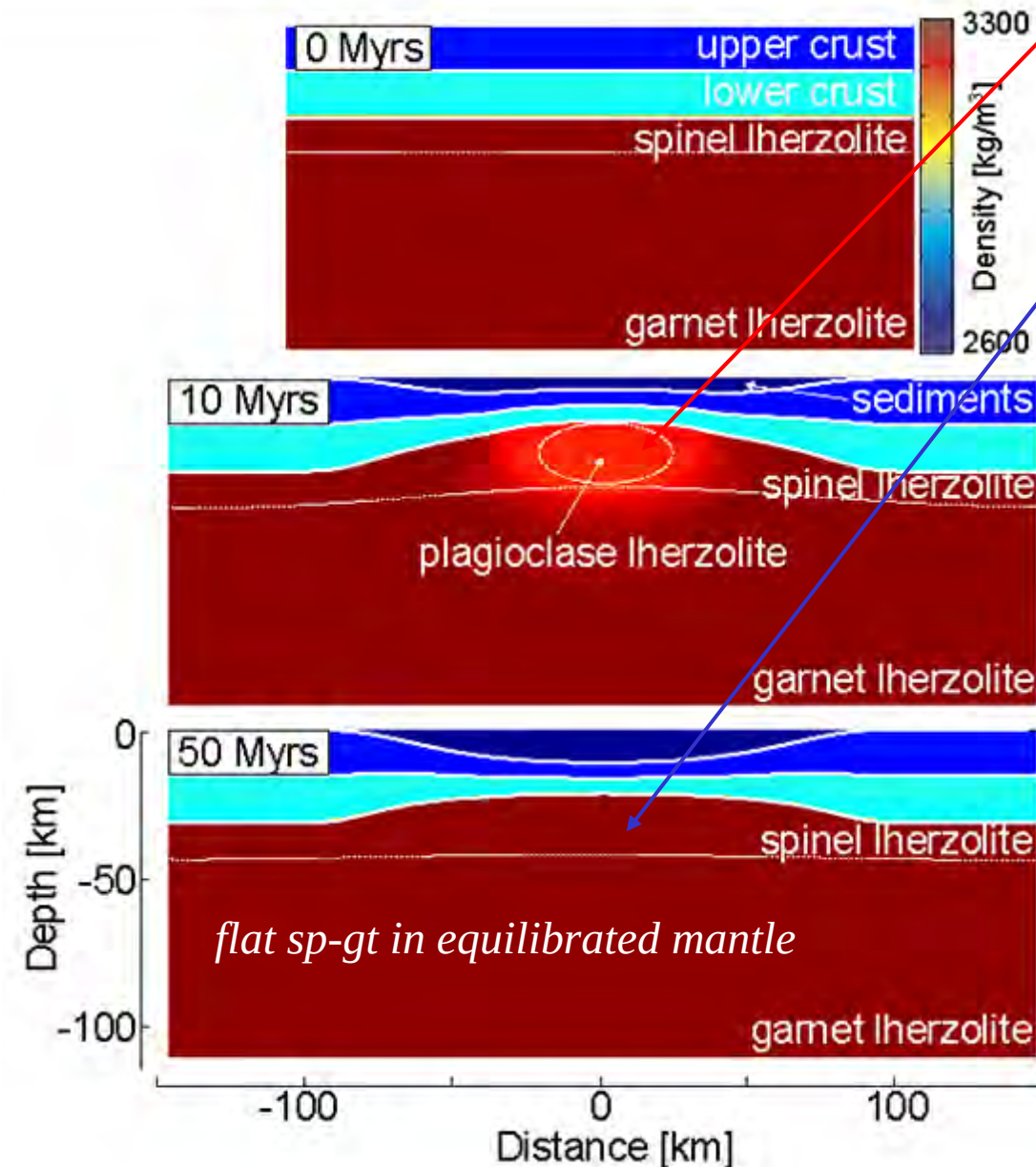
(Figure 8 of Kaus et al., 2005)

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 $\rho_0=2700 \text{ kgm}^{-3}$ and the lower a T -dependent density with $\rho_0=2900 \text{ kgm}^{-3}$. 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>).

plagioclase → spinel → garnet
herzolite transitions

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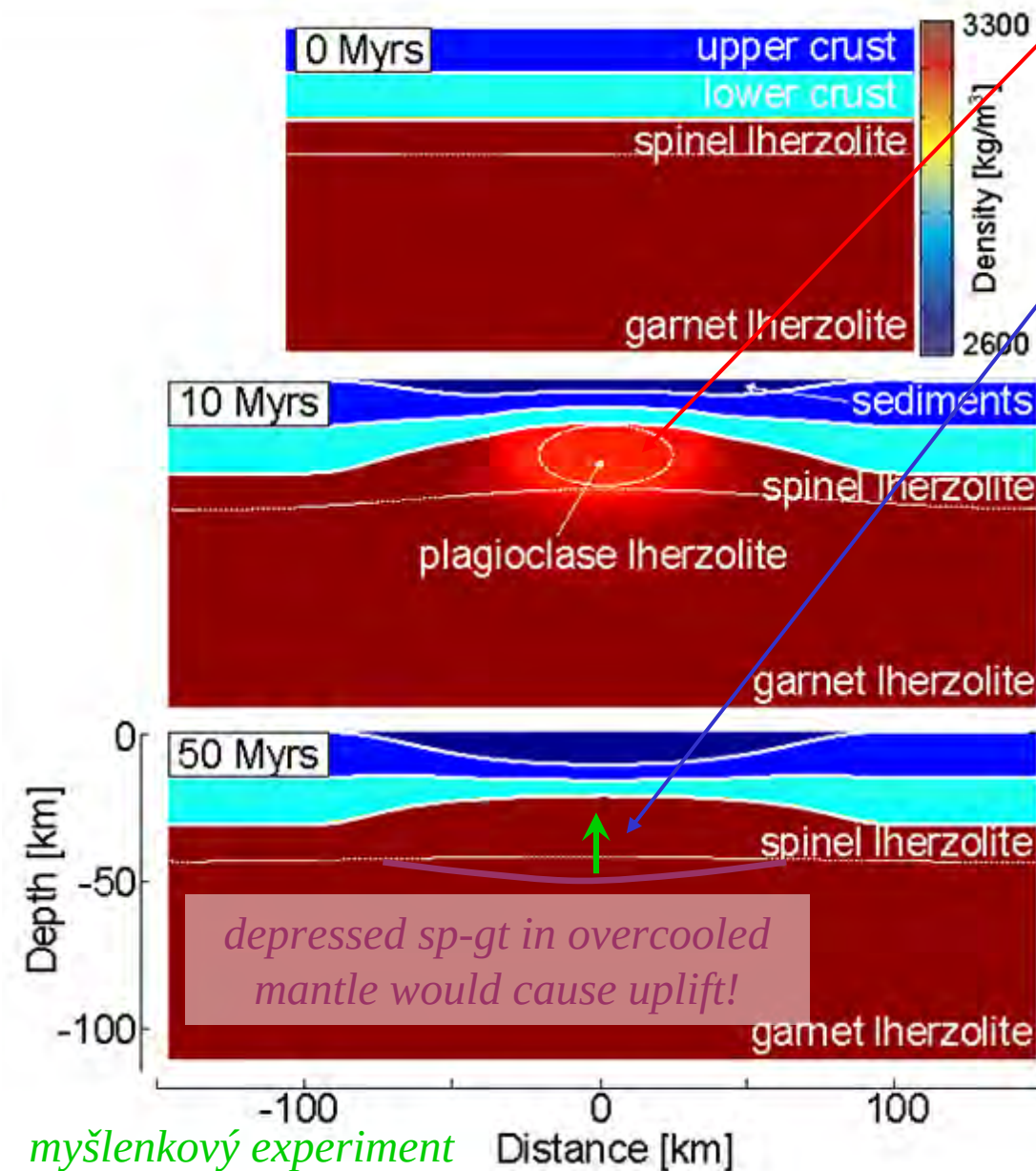
Results of 2-D computations with phase transitions activated in the mantle only (MOR-model). The maximum stretching factor in the center of the basin is 3. The upper crust has a T -dependent density with $q_0=2700 \text{ kgm}^{-3}$ and the lower a T -dependent density with $q_0=2900 \text{ kgm}^{-3}$. 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)

plagioclase → spinel → garnet
herzolite transitions

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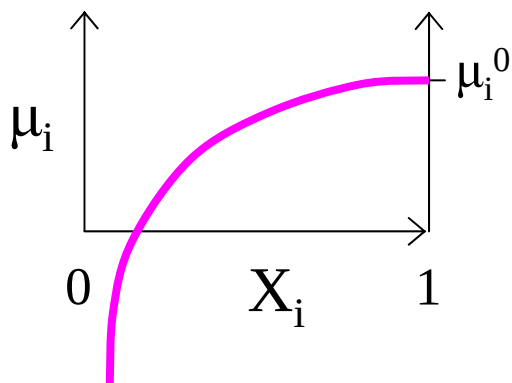
(Figure 8 of Kaus et al., 2005)

A Useful Rule: “Garnet Eats Everything”

„Granát sní všechno.“

$$\mu_i = \mu_i^0 + nRT \ln a_i$$

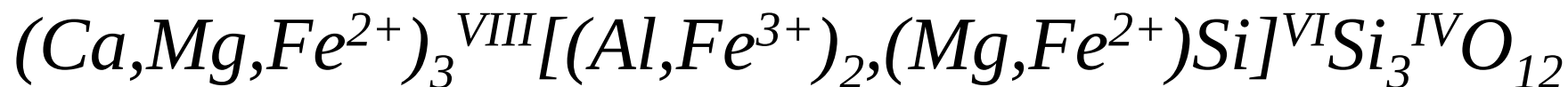
$$a_i \leq 1 \rightarrow RT \ln a_i \leq 0$$



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

Complex solutions have expanded stability fields.

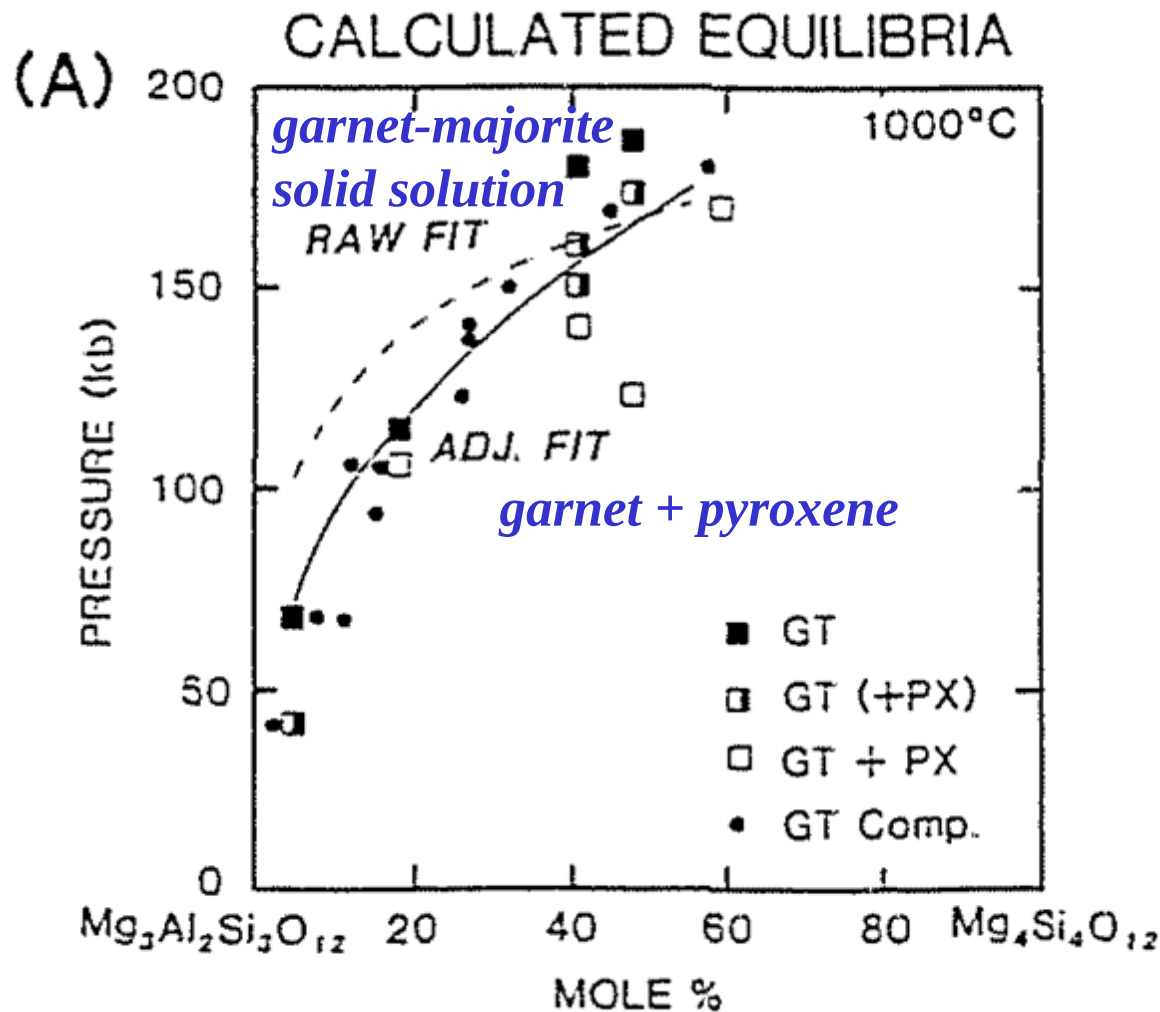
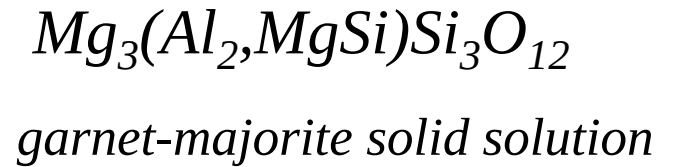
large entropy
of mixing



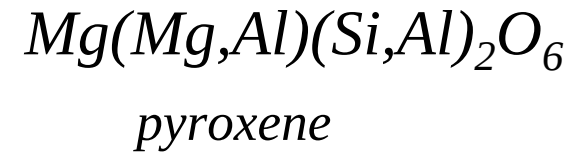
(a simple Ca-Mg-Fe garnet-majorite solid solution)

Thus, phase transitions involving garnet tend to be very broad.

eclogite → garnetite transition



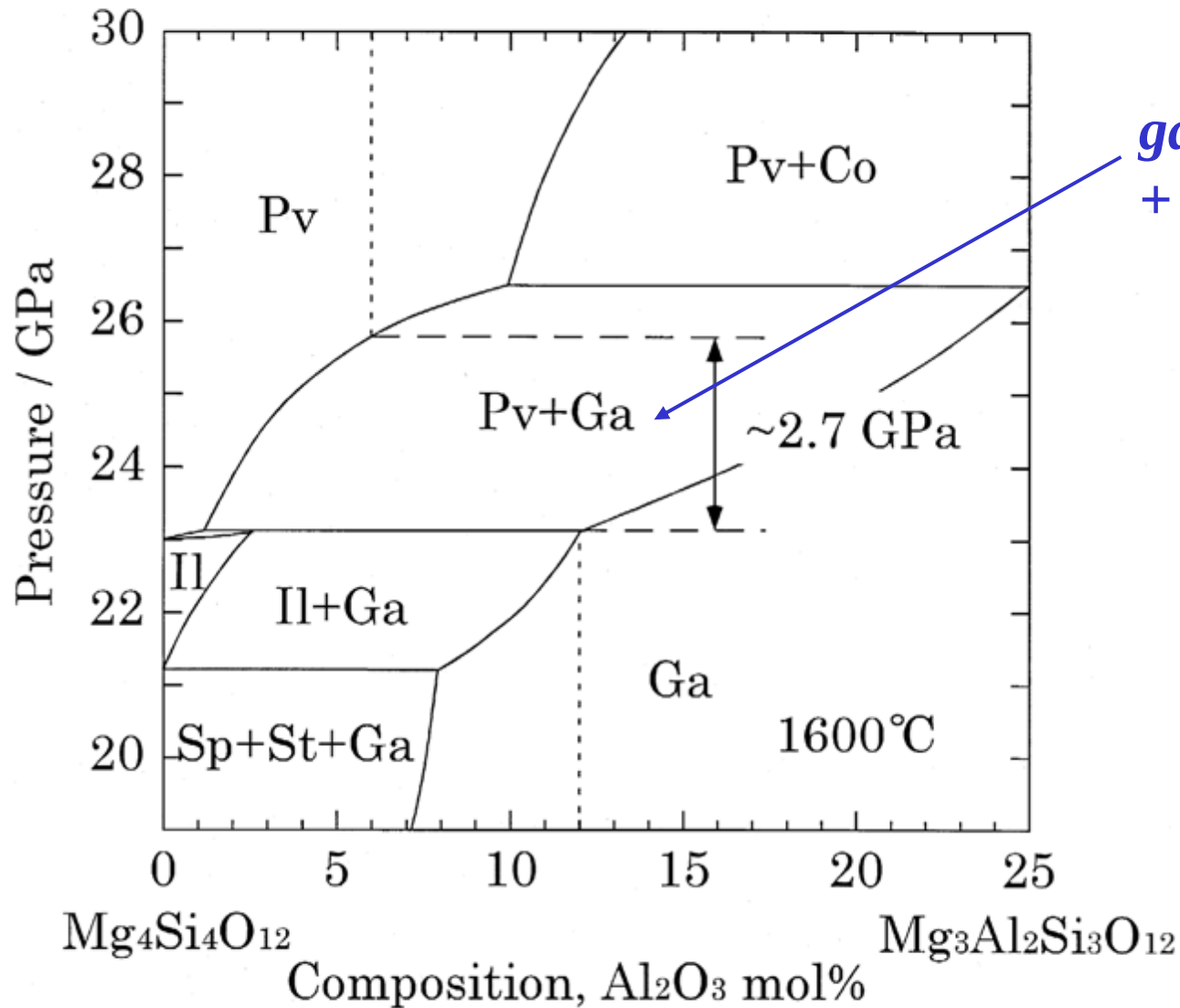
+



[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

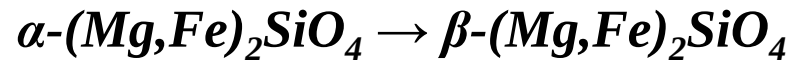
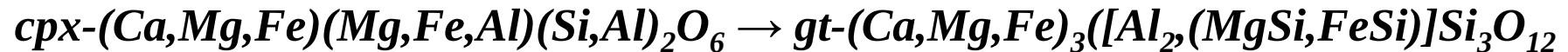


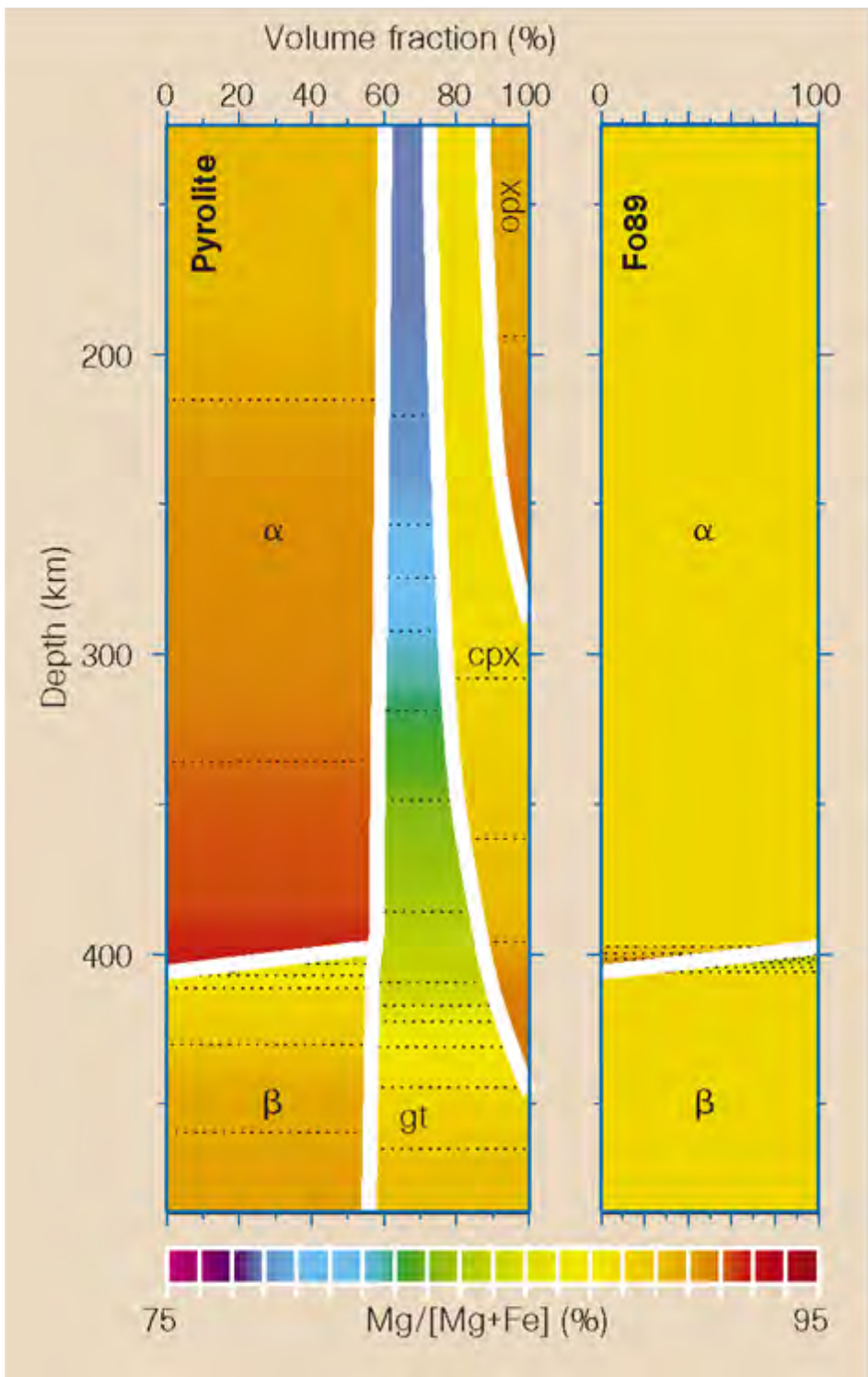
Transition sequence of majorite garnet in pyrolite mantle at 1600°C as a function of pressure. Dotted lines indicate approximate compositions of garnet and perovskite in the transition zone and lower mantle, respectively (see Section 3.4). Dashed lines show pressure interval of about 2.7 GPa for the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

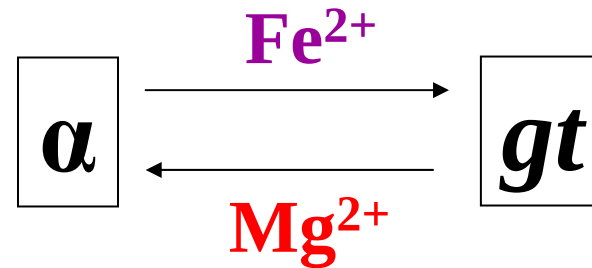
Two Phase Transitions Can Interact by Cation Exchange

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

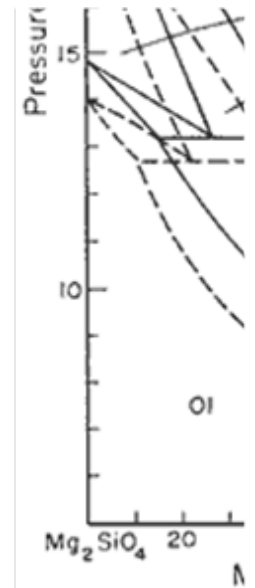




Mg-Fe exchange between olivine and garnet:



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

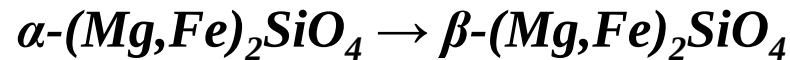
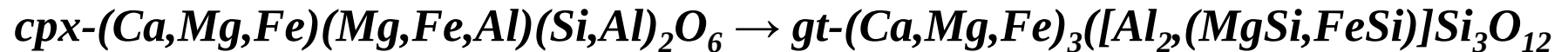


Equilibrium mineral proportions and compositions as functions of mantle depth, for $(\text{Mg}_{0.89}\text{Fe}_{0.11})_2\text{SiO}_4$ olivine in isolation (Fo89) and for a model (pyrolite) mantle composition. Mineral proportions are as volume fraction, shown by bold white lines; compositions are in terms of $\text{Mg}/[\text{Mg}+\text{Fe}]$, and are shown by colours and by dotted contours at 1% intervals. With increasing depth, olivine (α) transforms to wadsleyite (β) 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.)

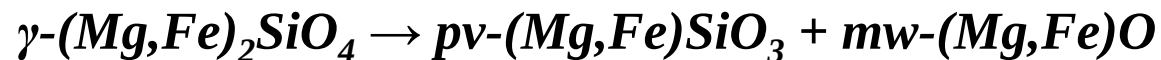
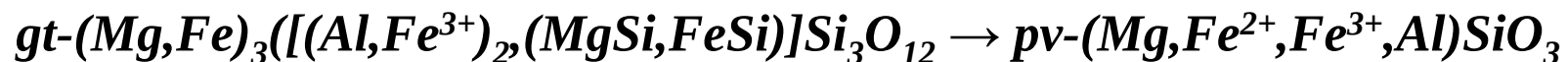
(Figure 1 of Bina, 1998; after Irifune and Isshiki, 1998)

Two Phase Transitions Can Interact by Cation Exchange

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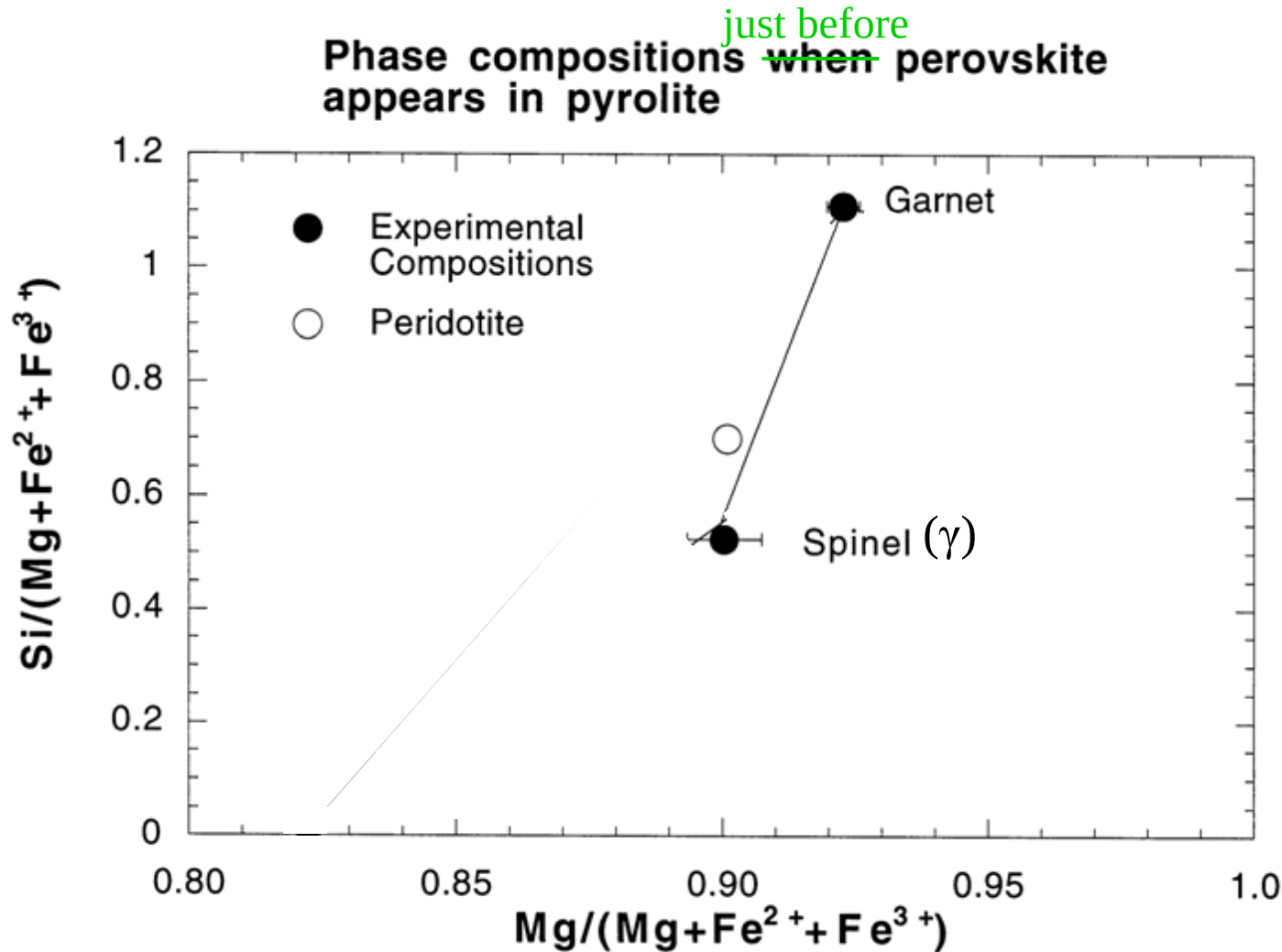


Example 2: the olivine $\gamma \rightarrow \text{pv} + \text{mw}$ transition and the gt $\rightarrow$ pv transition



ringwoodite (γ) 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.

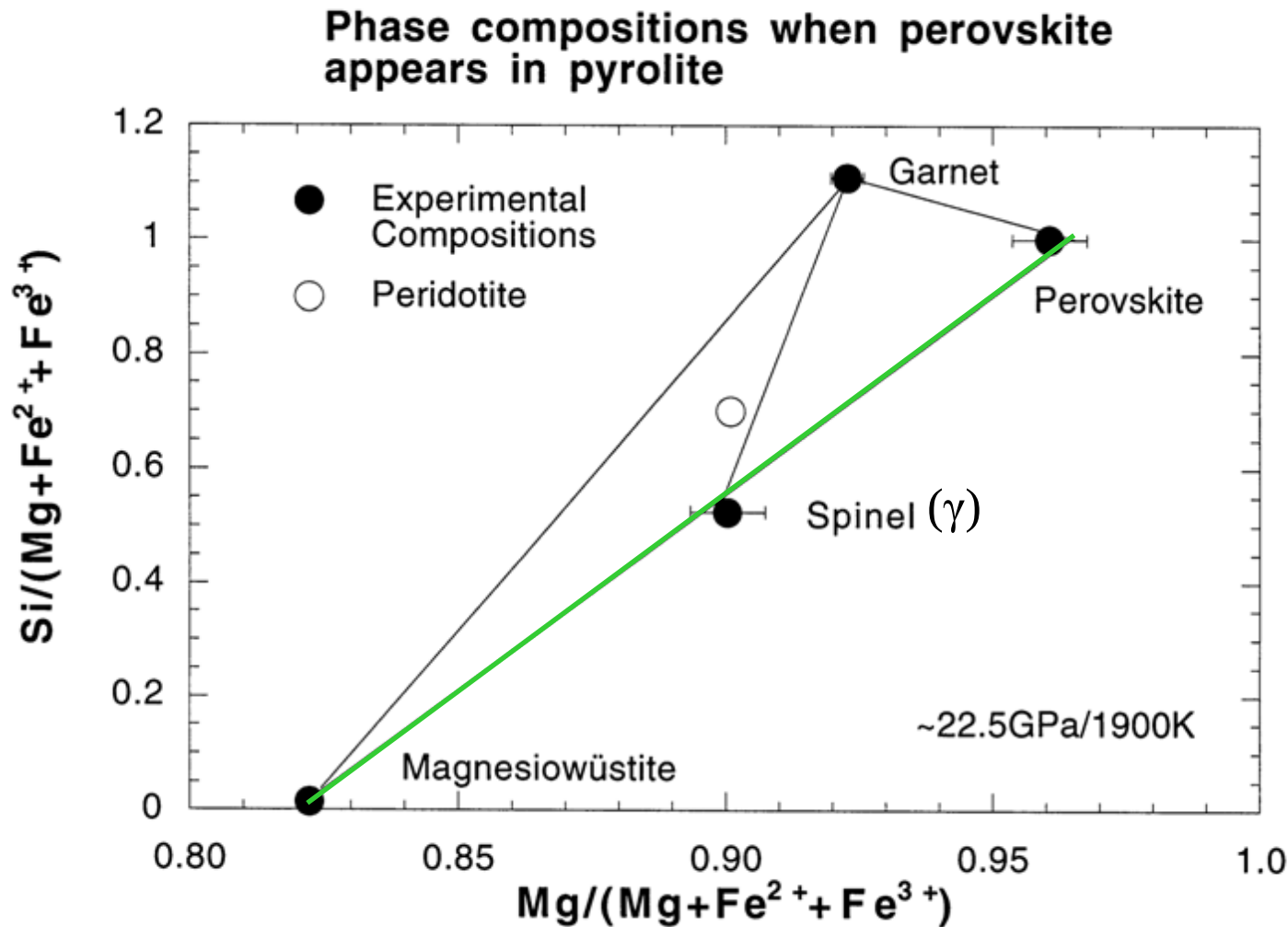


Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.

(after Figure 4 of Wood, 2000)

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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.

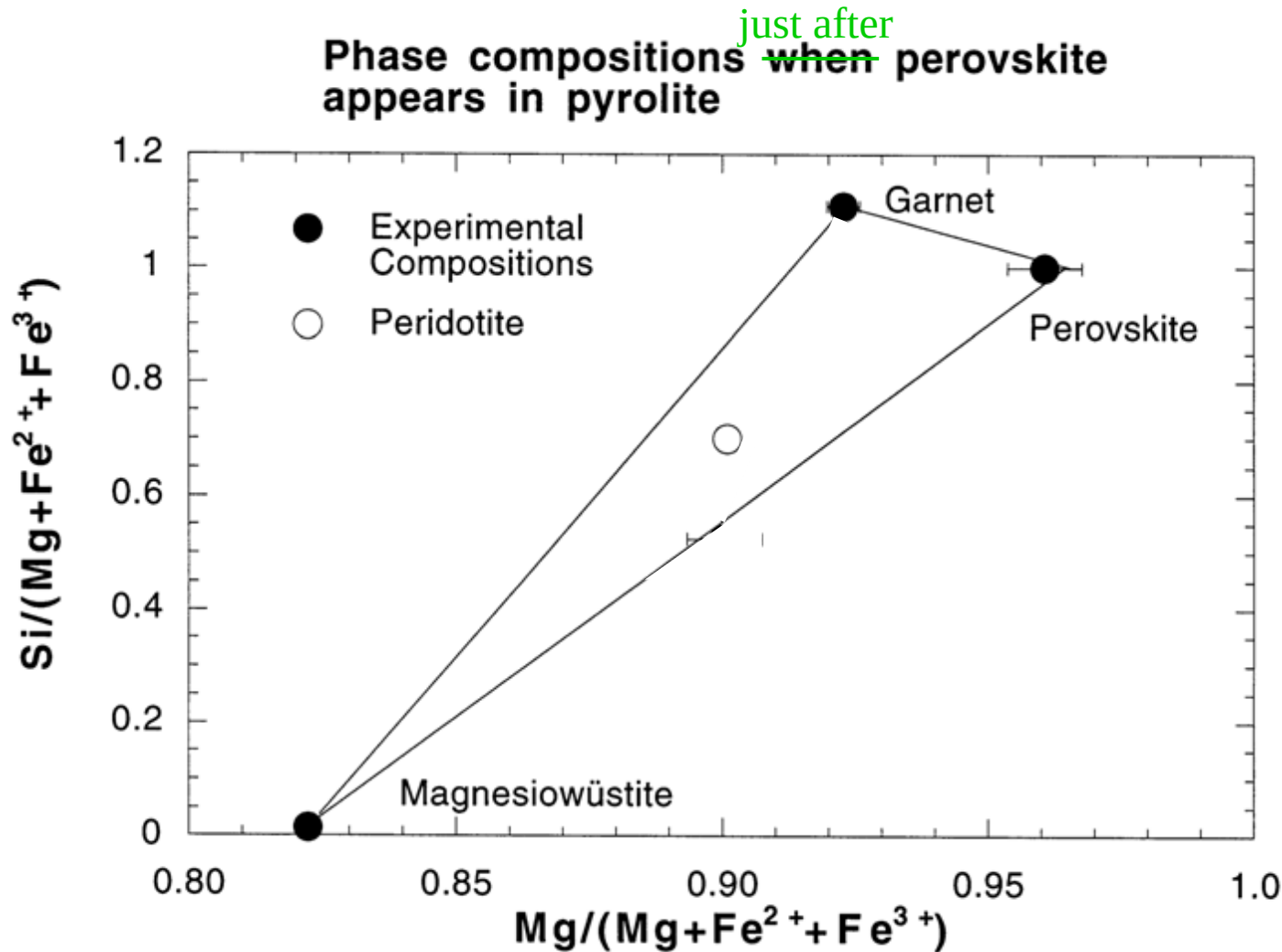


Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.

(Figure 4 of Wood, 2000)

ringwoodite (γ) 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.

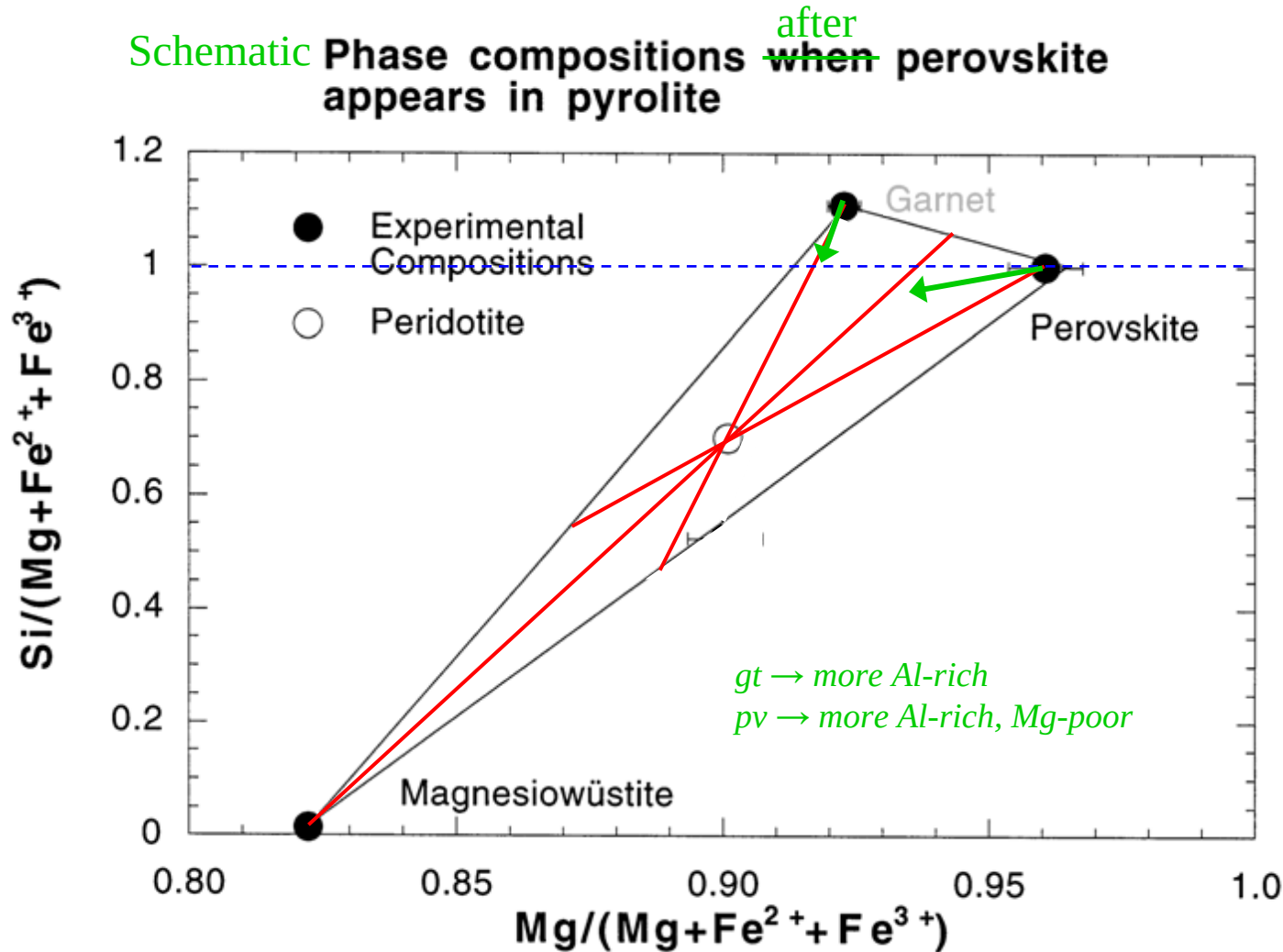


Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.

(after Figure 4 of Wood, 2000)

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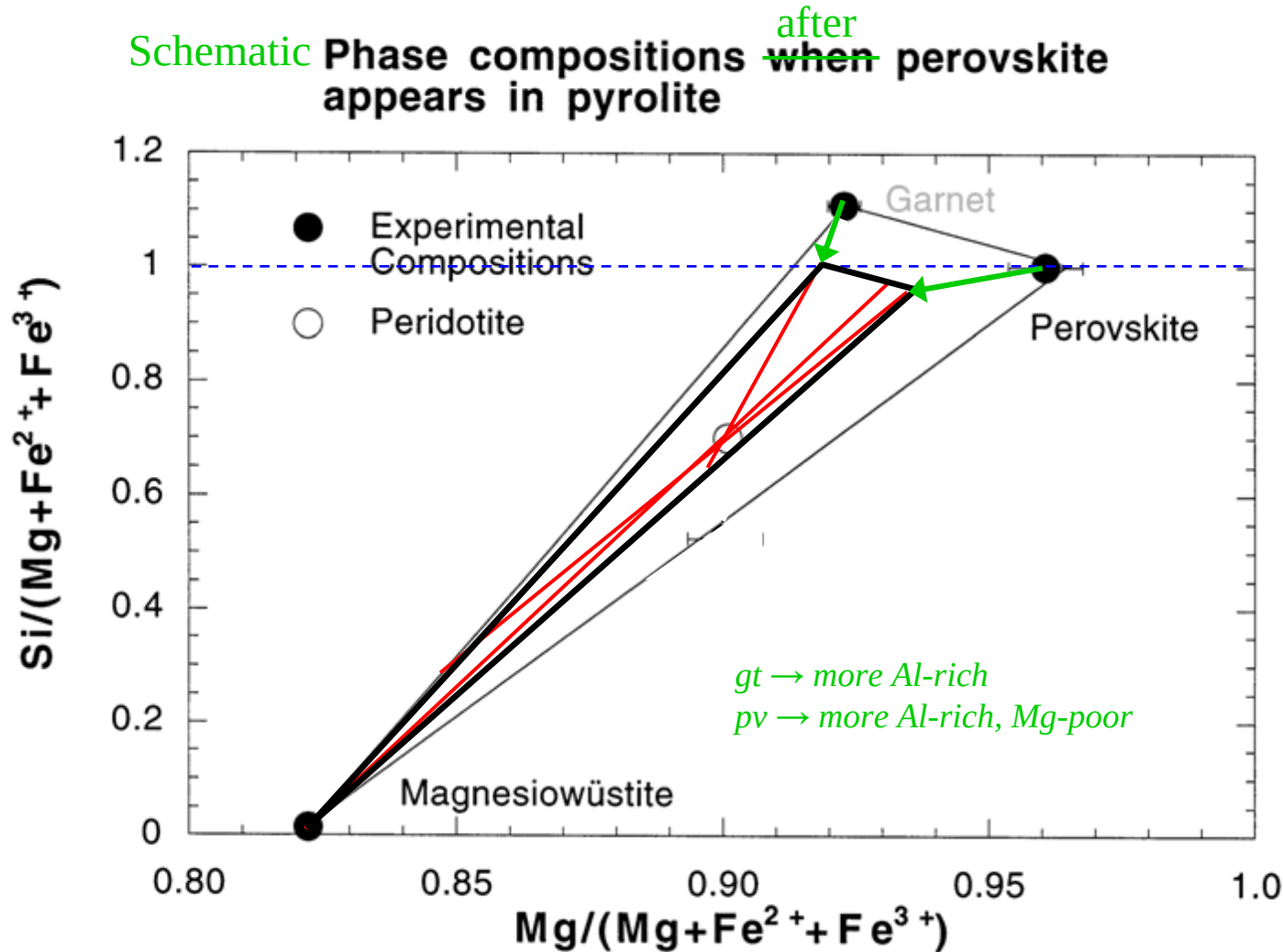


Phase compositions in MORB-pyrolite just at the point of appearance of Mg-perovskite (about 22.5 GPa/1900K). Note that magnesiowüstite (MW) is colinear with spinel and perovskite, indicating that the spinel breakdown reaction is pseudo-univariant as shown in Fig. 1A. Error bars are two standard errors.

(after Figure 4 of Wood, 2000)

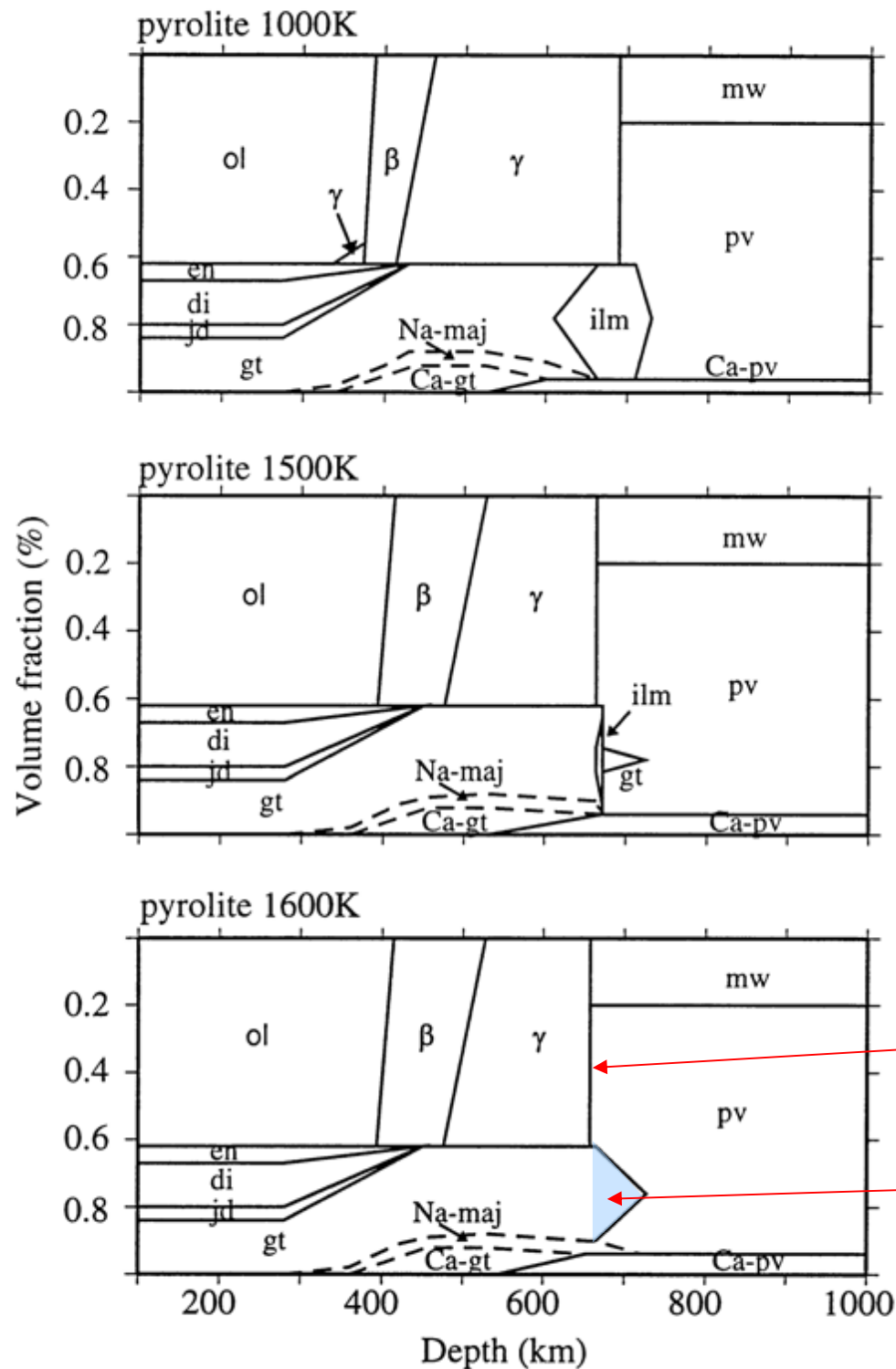
ringwoodite (γ) plus garnet $\rightarrow$ silicate perovskite plus magnesiowüstite (ferropericlase) transition

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)



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

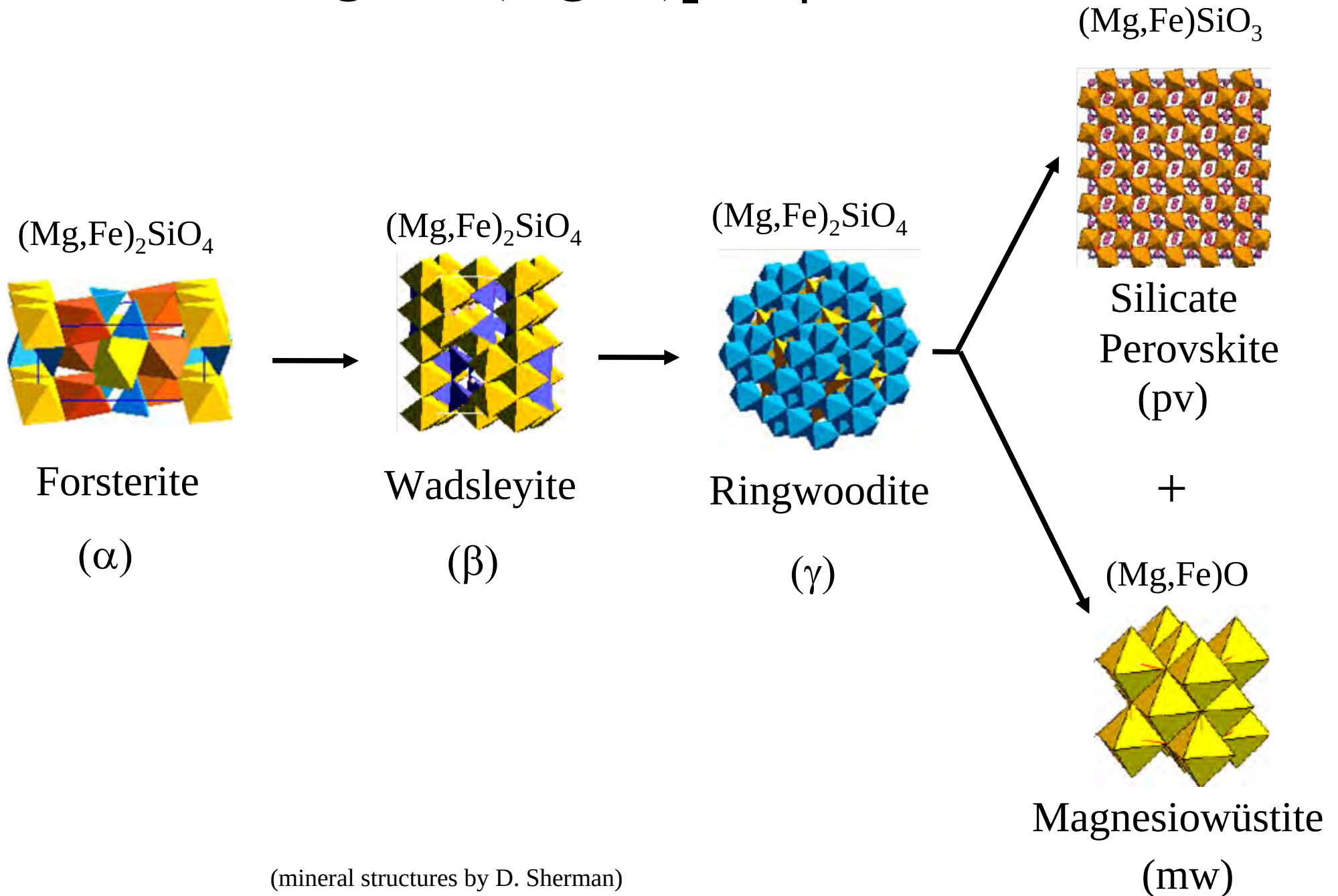
Volumic proportions of minerals and phases present in the pyrolite composition as a function of depth, along the 1000 K (top) and 1500 K (middle) and 1600 K (bottom) adiabats. Dashed lines give the proportions of 'virtual phases', which are part of the garnet solid solution. en: enstatite; di: diopside; jd: jadeite; Ca-gt: Ca-garnet; Na-maj: Na-majorite; other symbols are defined in Fig. 1 and Fig. 2.

$\gamma \rightarrow pv + mw$

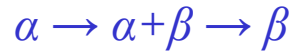
$gt \rightarrow pv$

(Figure 3 of Vacher et al., 1998)

Phase Changes in $(\text{Mg,Fe})_2\text{SiO}_4$ Olivine



Equilibrium Olivine Phase Relations

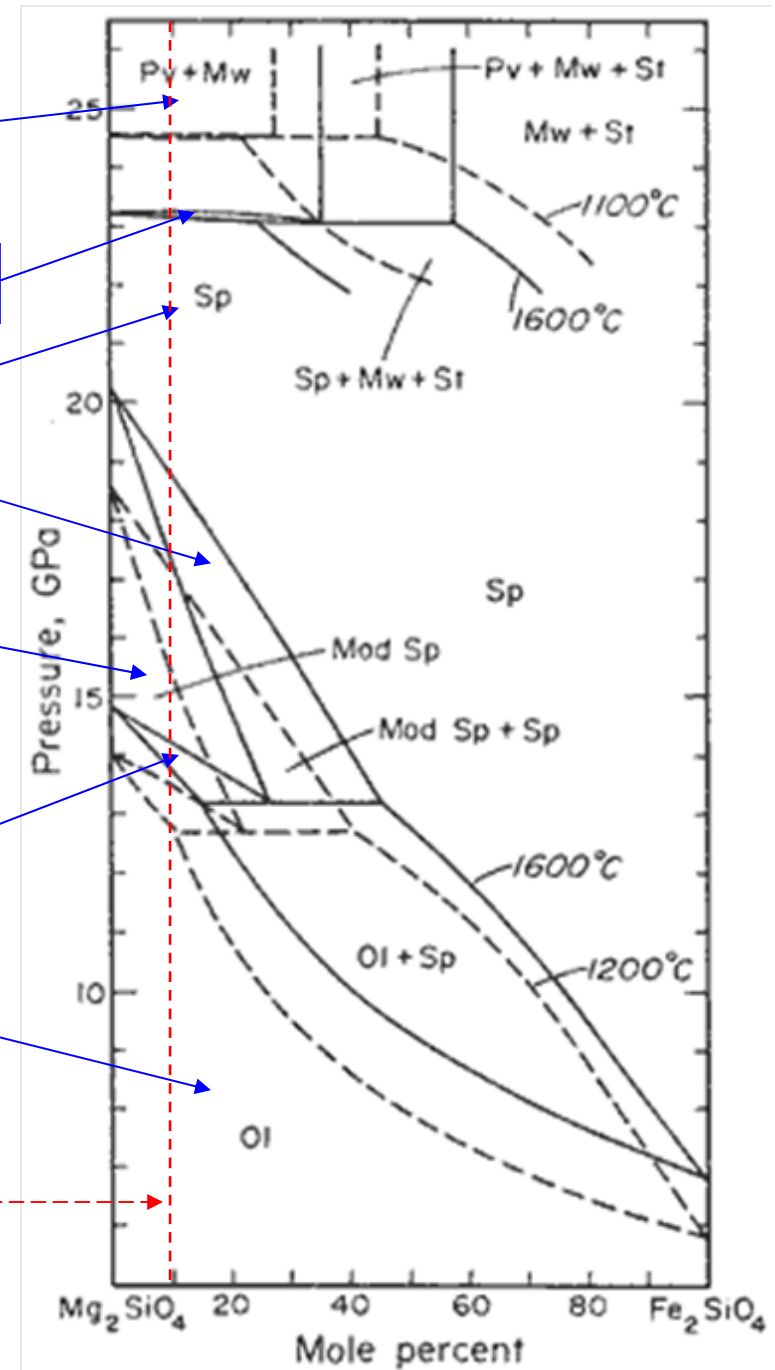


$\alpha = \text{Ol}$
 $\beta = \text{Mod Sp}$
 $\gamma = \text{Sp}$

660 km discontinuity

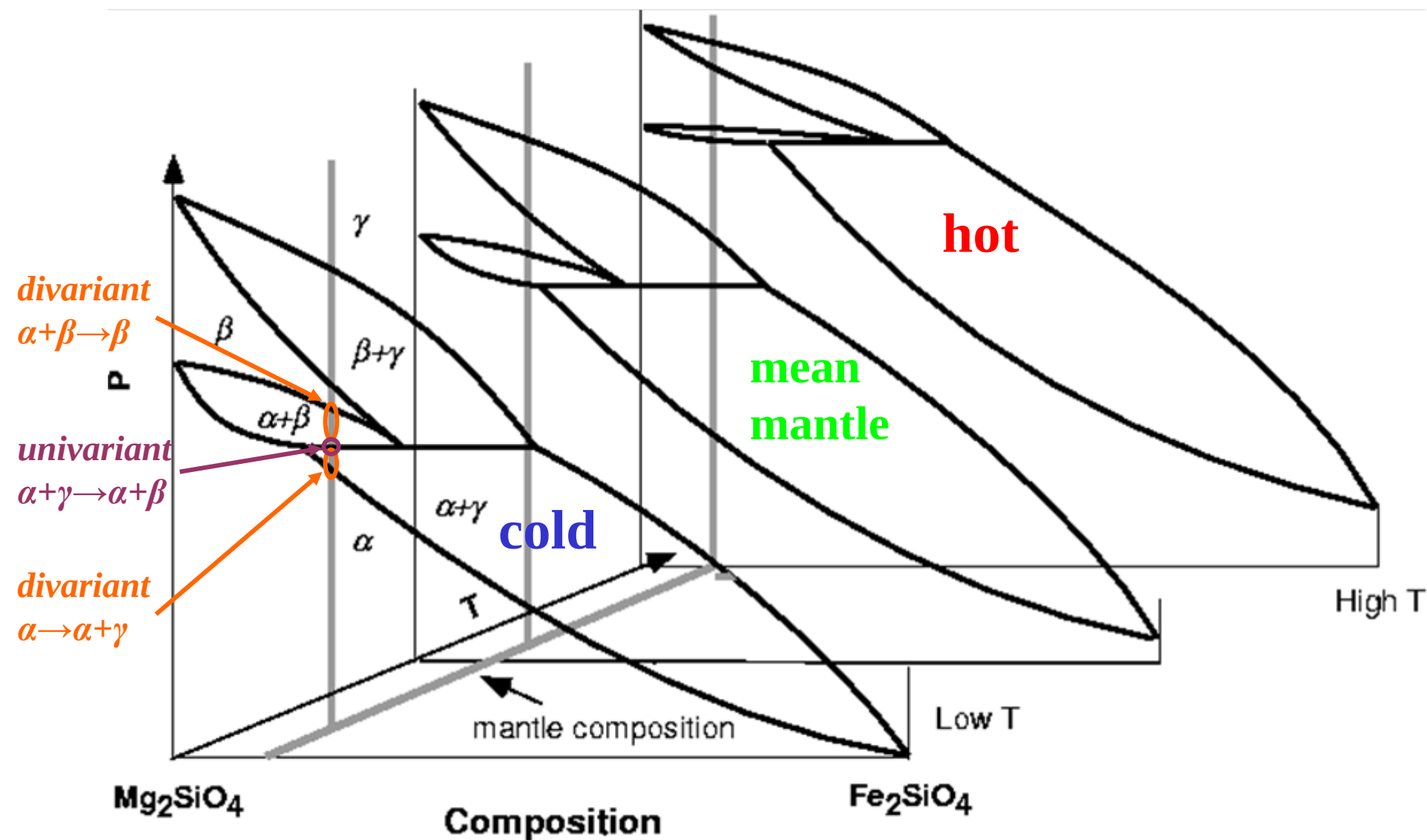
410 km discontinuity

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



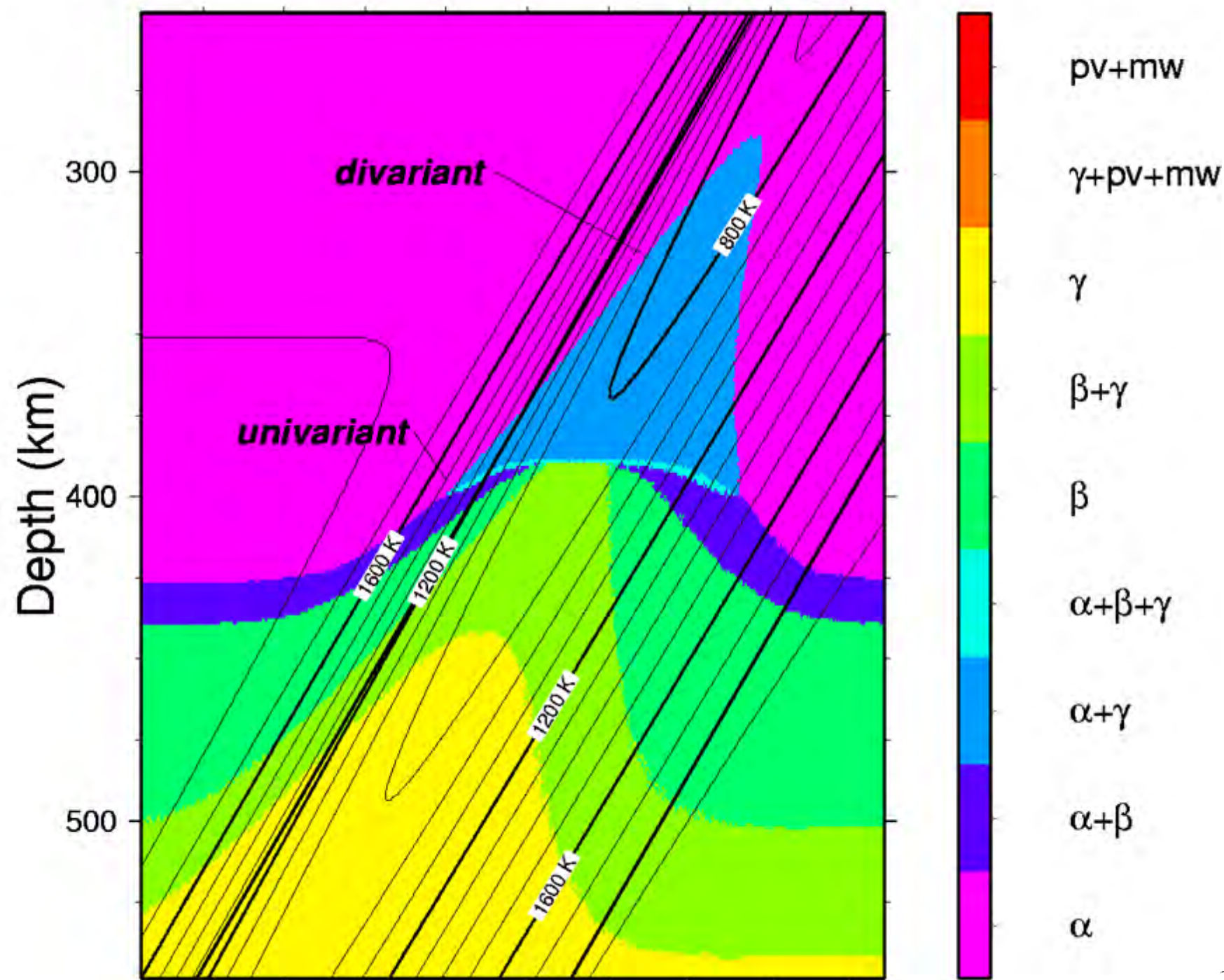
(Figure 16 from Presnall [1995])

Equilibrium Olivine α - β - γ Polymorph Phase Relations



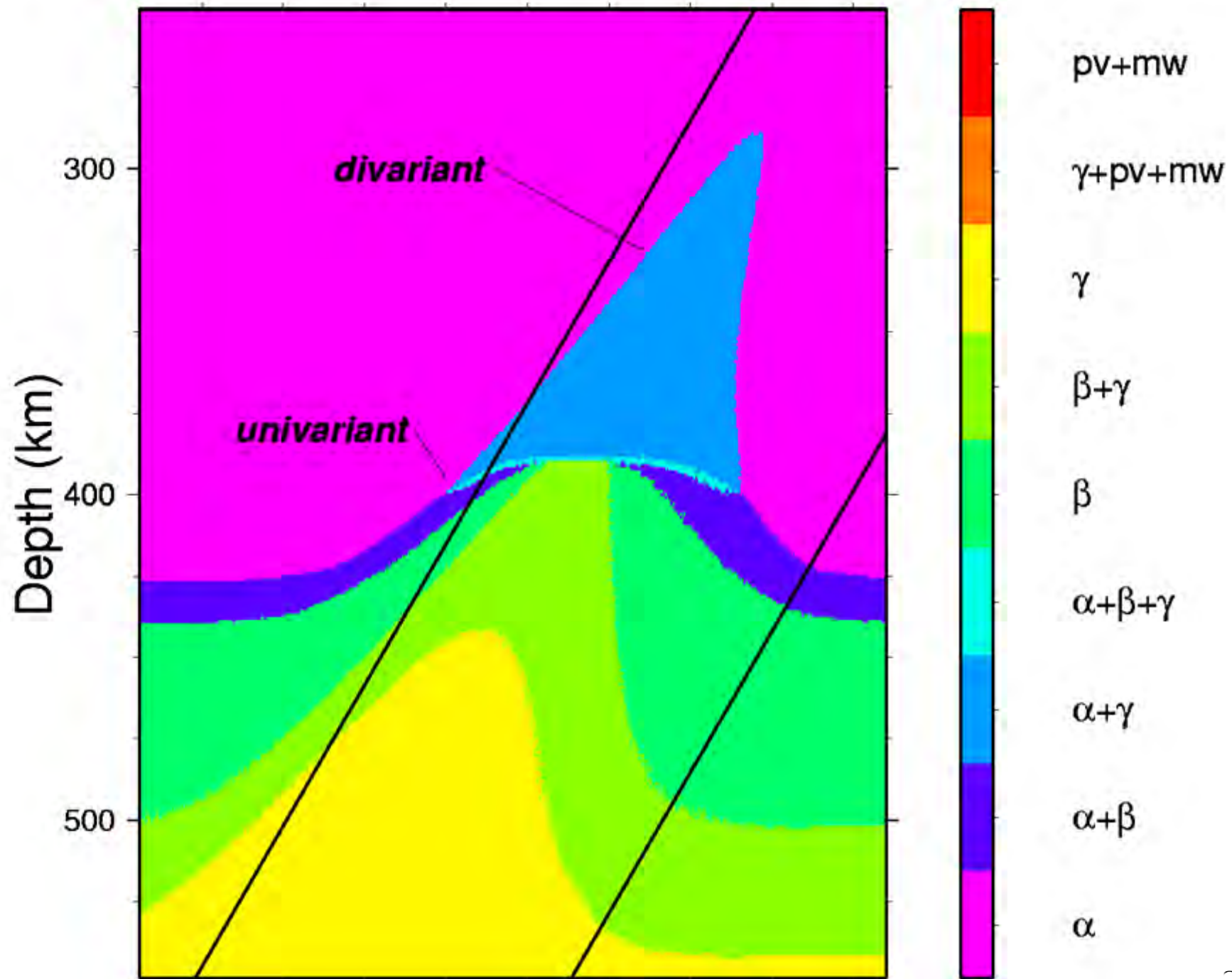
[after Helffrich & Bina, 1994]

$(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ Equilibrium Phase Assemblages



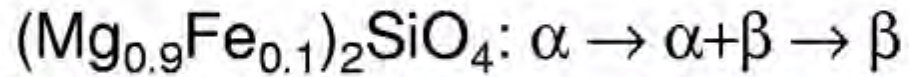
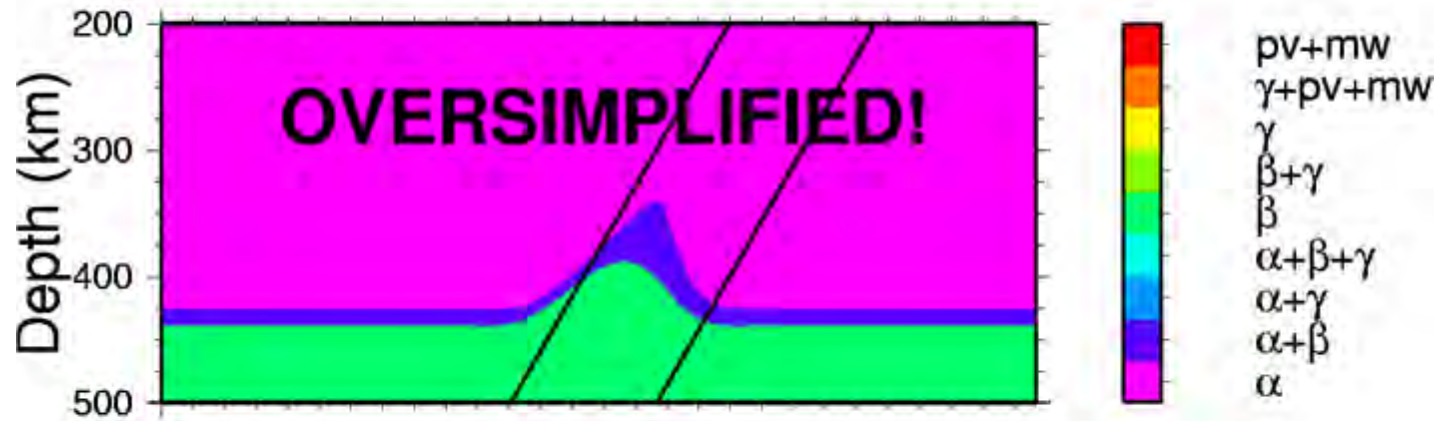
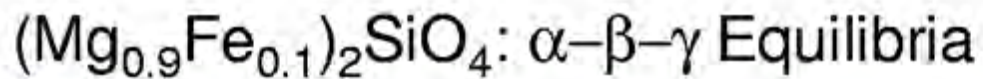
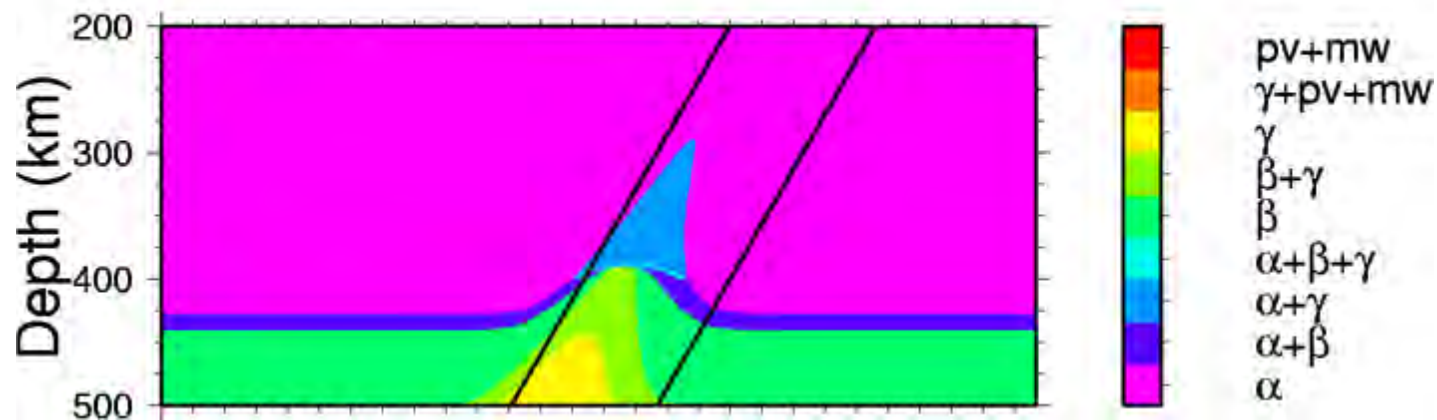
(Figure from Bina, 2002)

$(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ Equilibrium Phase Assemblages



(Figure from Bina, 2002)

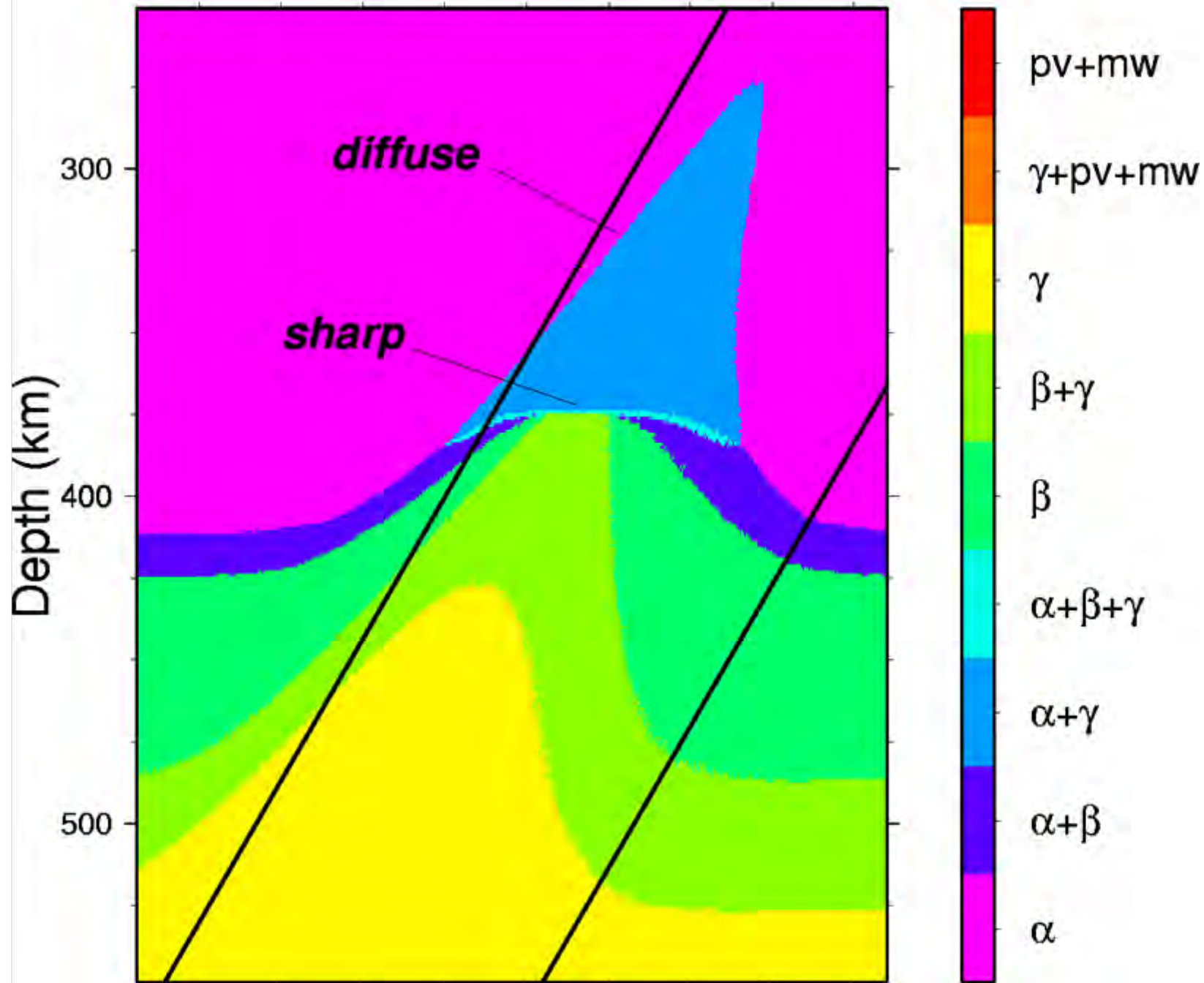
410-km seismic discontinuity uplifted in subduction zones



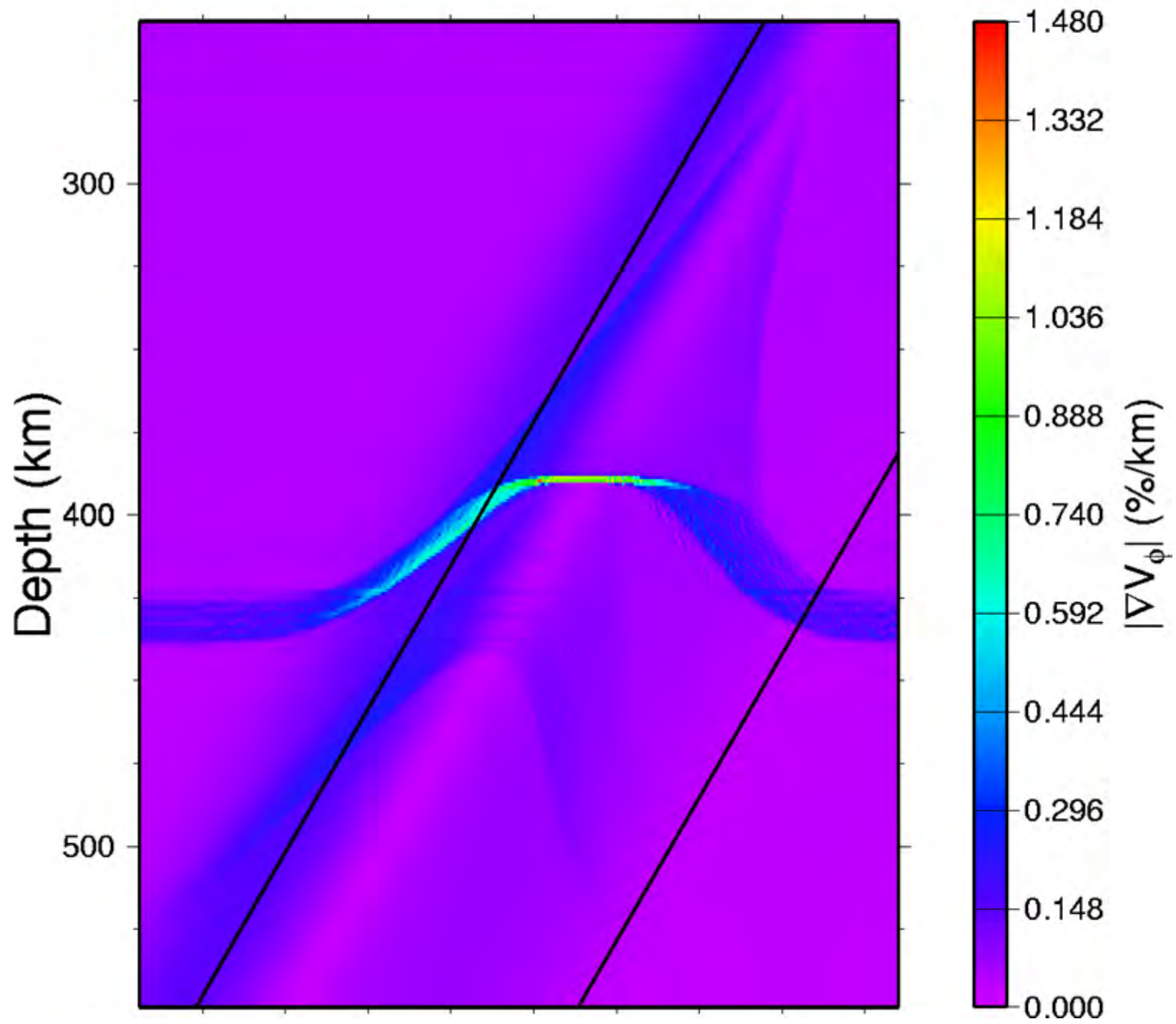
(Figure from Bina, 2002)

$(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ Equilibria

(Figure 3 of Bina [2003])

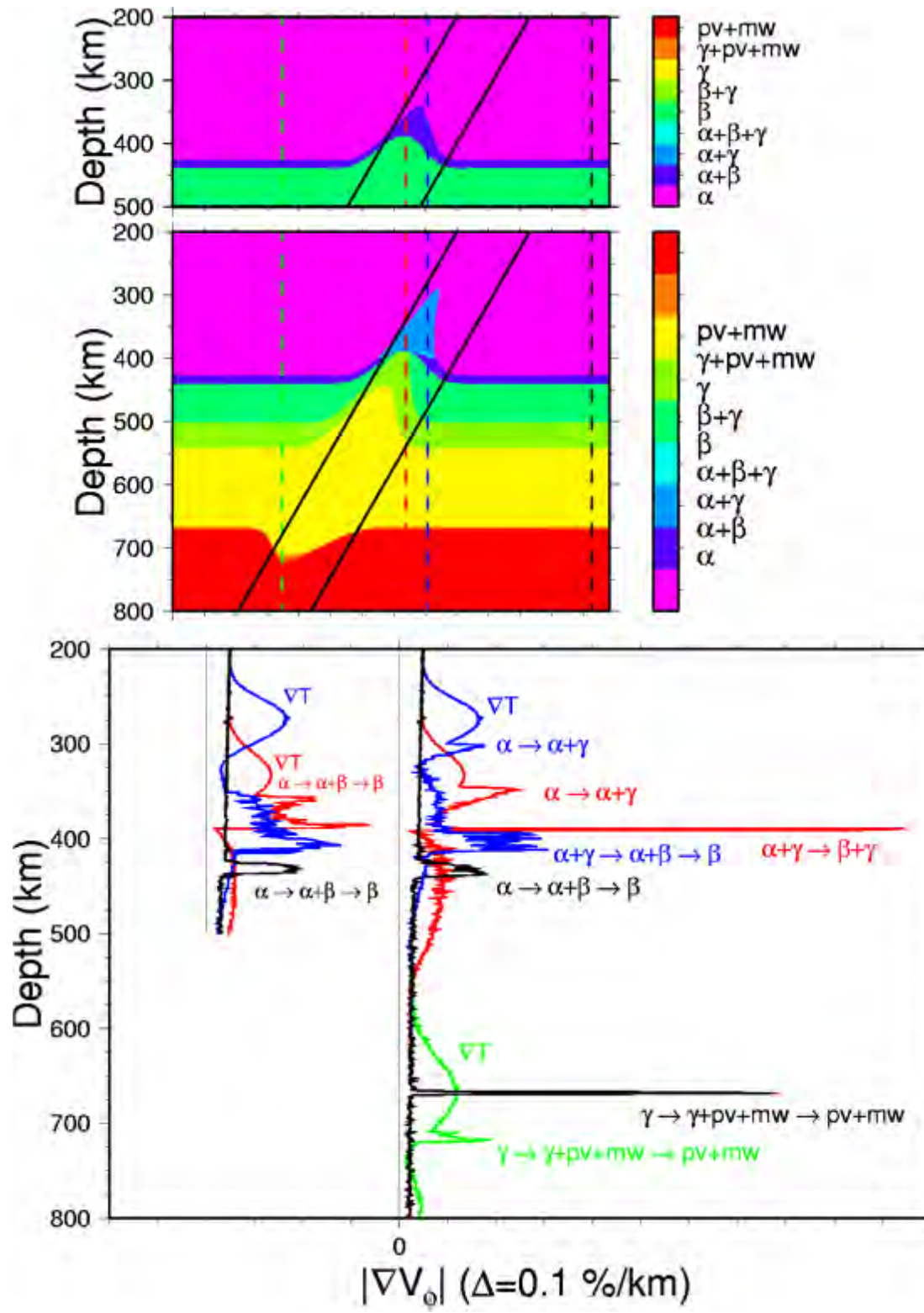


Acoustic Velocity Gradients



(Figure from Bina, 2002)

Seismic Reflectivity



(Figure from Bina, 2002)