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

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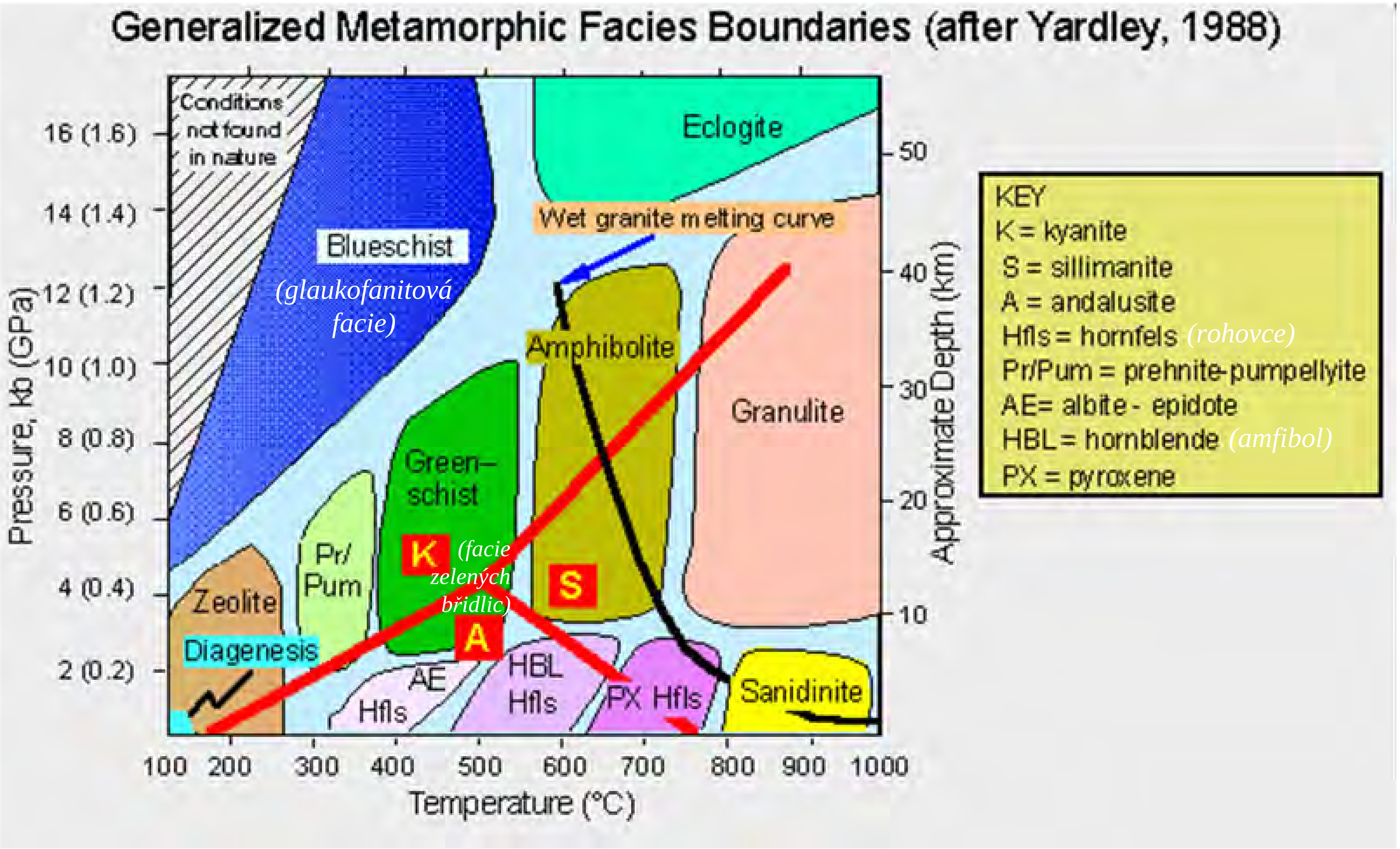
Geobarometry and Geothermometry

Petrology allows us to estimate the range of pressure *and* temperature *of equilibration by observing the coexisting mineral species.*

metamorfní facie (stupně metamorfózy)



(from J. Ahern)

(C.Bina, 9/2011)

metamorfní facie (stupně metamorfózy)

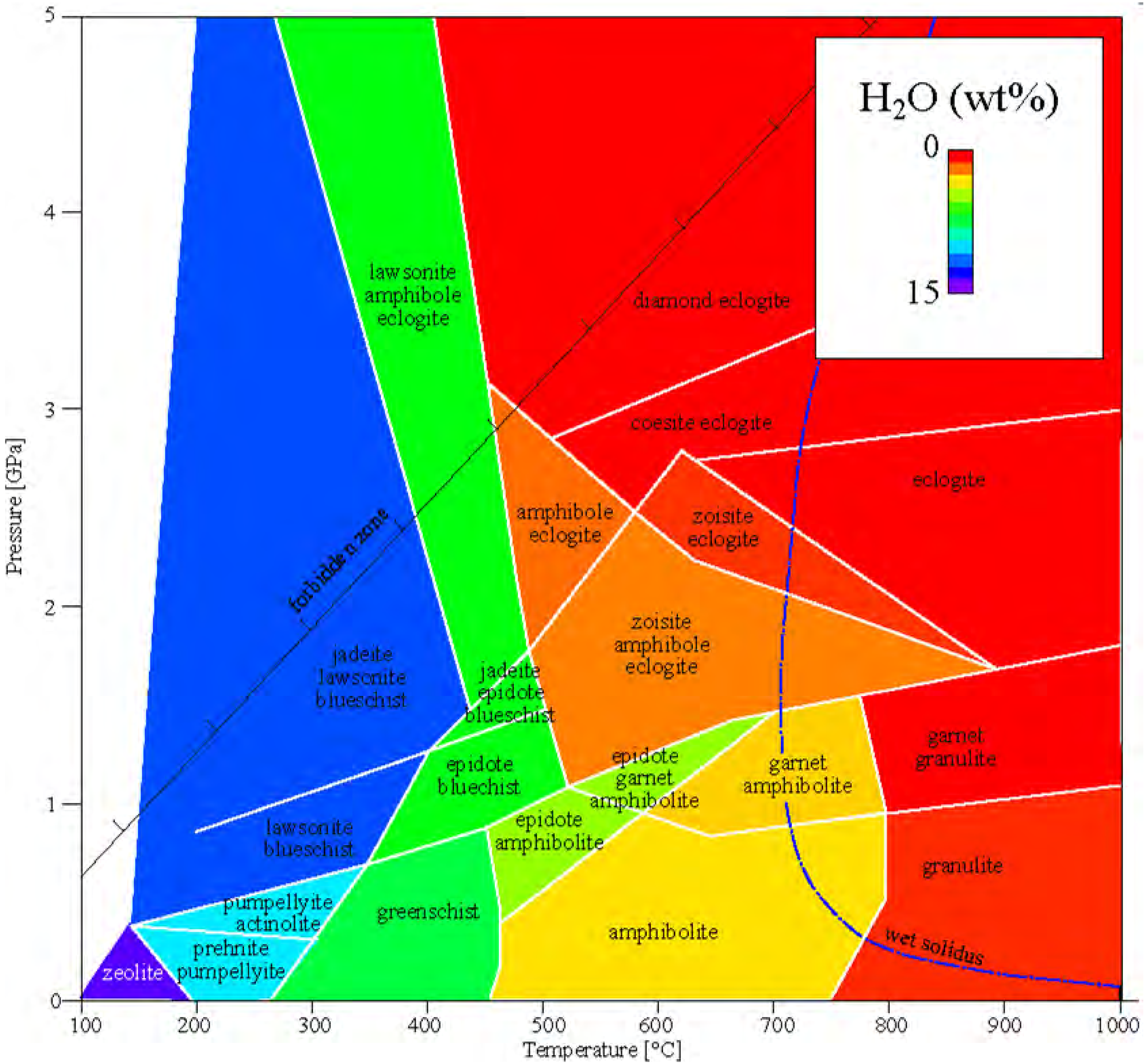
Table 25-1. Definitive Mineral Assemblages of Metamorphic Facies

Facies	Definitive Mineral Assemblage in Mafic Rocks
Zeolite	zeolites: especially laumontite, wairakite, analcime
Prehnite-Pumpellyite	prehnite + pumpellyite (+ chlorite + albite)
Greenschist	chlorite + albite + epidote (or zoisite) + quartz ± actinolite
Amphibolite	hornblende + plagioclase (oligoclase-andesine) ± garnet
Granulite	orthopyroxene (+ clinopyroxene + plagioclase ± garnet ± hornblende)
Blueschist	glaucophane + lawsonite or epidote (+albite ± chlorite)
Eclogite	pyrope garnet + omphacitic pyroxene (± kyanite)
Contact Facies	Mineral assemblages in mafic rocks of the facies of contact metamorphism do not differ substantially from that of the corresponding regional facies at higher pressure.

After Spear (1993)

Table 25.1. The definitive mineral assemblages that characterize each facies (for mafic rocks). Winter (2010) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

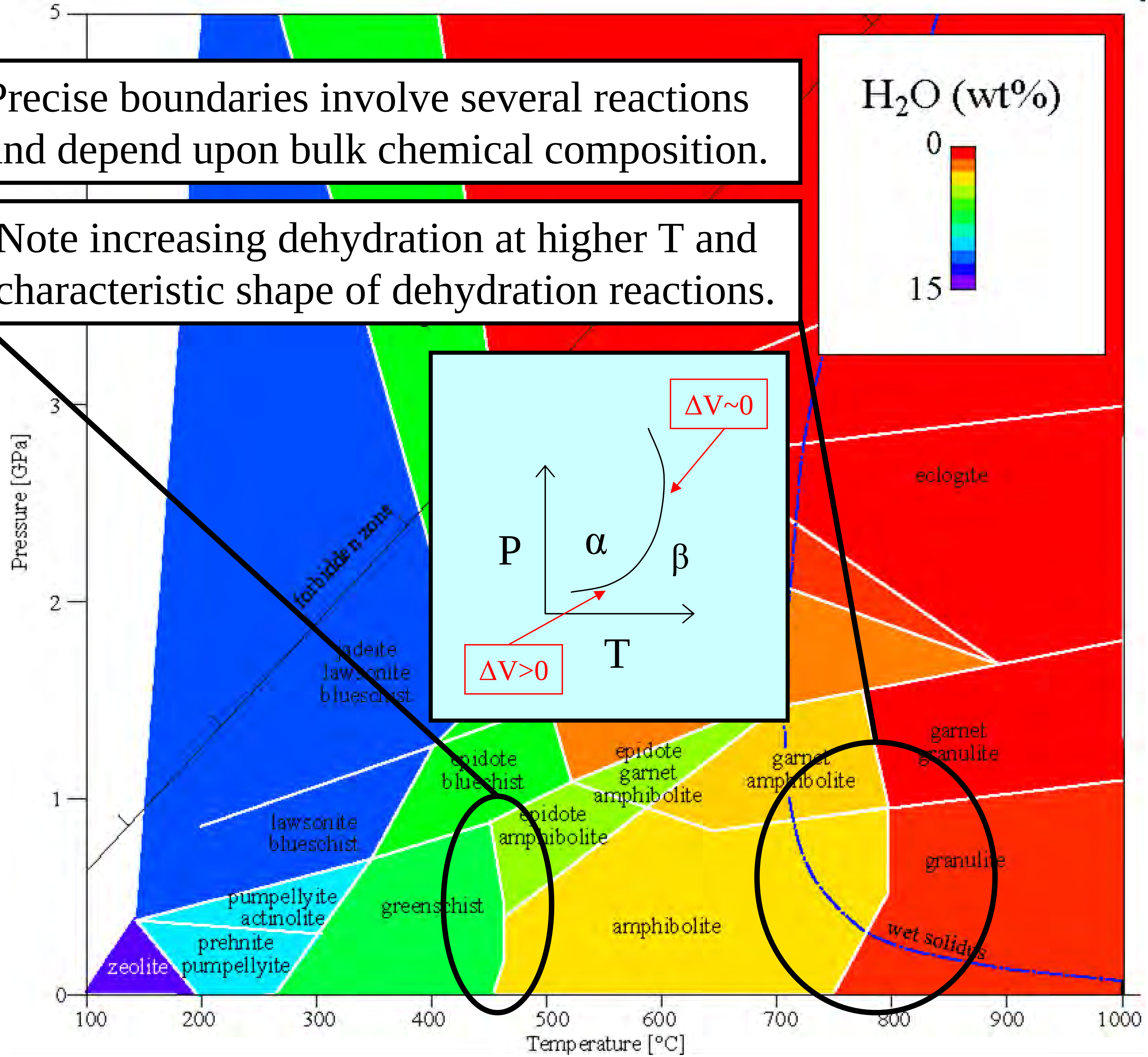
podrobnější metamorfní facie (stupně metamorfózy)



(from B. Hacker)

(C.Bina, 9/2011)

podrobnější metamorfní facie (stupně metamorfózy)



(facies boundaries from B. Hacker)

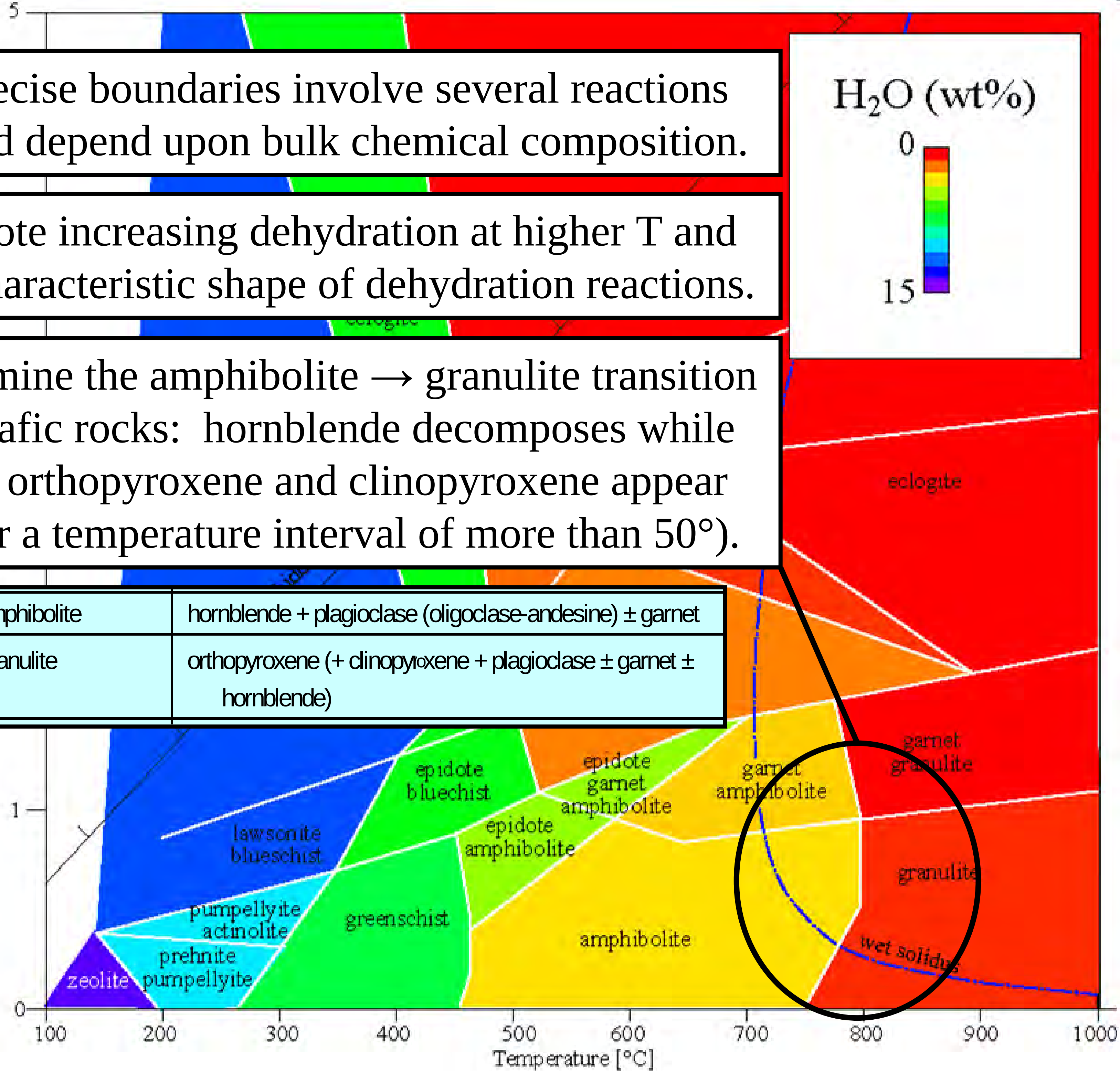
(C.Bina, 9/2011)

Precise boundaries involve several reactions and depend upon bulk chemical composition.

Note increasing dehydration at higher T and characteristic shape of dehydration reactions.

Examine the amphibolite → granulite transition in mafic rocks: hornblende decomposes while both orthopyroxene and clinopyroxene appear (over a temperature interval of more than 50°).

Amphibolite	hornblende + plagioclase (oligoclase-andesine) ± garnet
Granulite	orthopyroxene (+ clinopyroxene + plagioclase ± garnet ± hornblende)



podrobnější metamorf... é metamorfózy)

(facies boundaries from B. Hacker)

(C.Bina, 9/2011)

The amphibolite → granulite transition in mafic rocks: hornblende decomposes while both orthopyroxene and clinopyroxene appear.

Note characteristic shape of dehydration reactions.

General form of reaction progress:

$hbl\text{-}(Ca,Na)_{2\text{–}3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$ +
$plag\text{-}(Na,Ca)(Al,Si)AlSi_2O_8$ →
$opx\text{-}(Mg,Fe)(Al,Mg,Fe)(Si,Al)_2O_6$ +
$cpx\text{-}(Ca,Na,Mg,Fe)(Al,Mg,Fe)(Si,Al)_2O_6$ +
$plag\text{-}(Na,Ca)(Al,Si)AlSi_2O_8$ + $fluid\text{-}H_2O{\cdot}F$

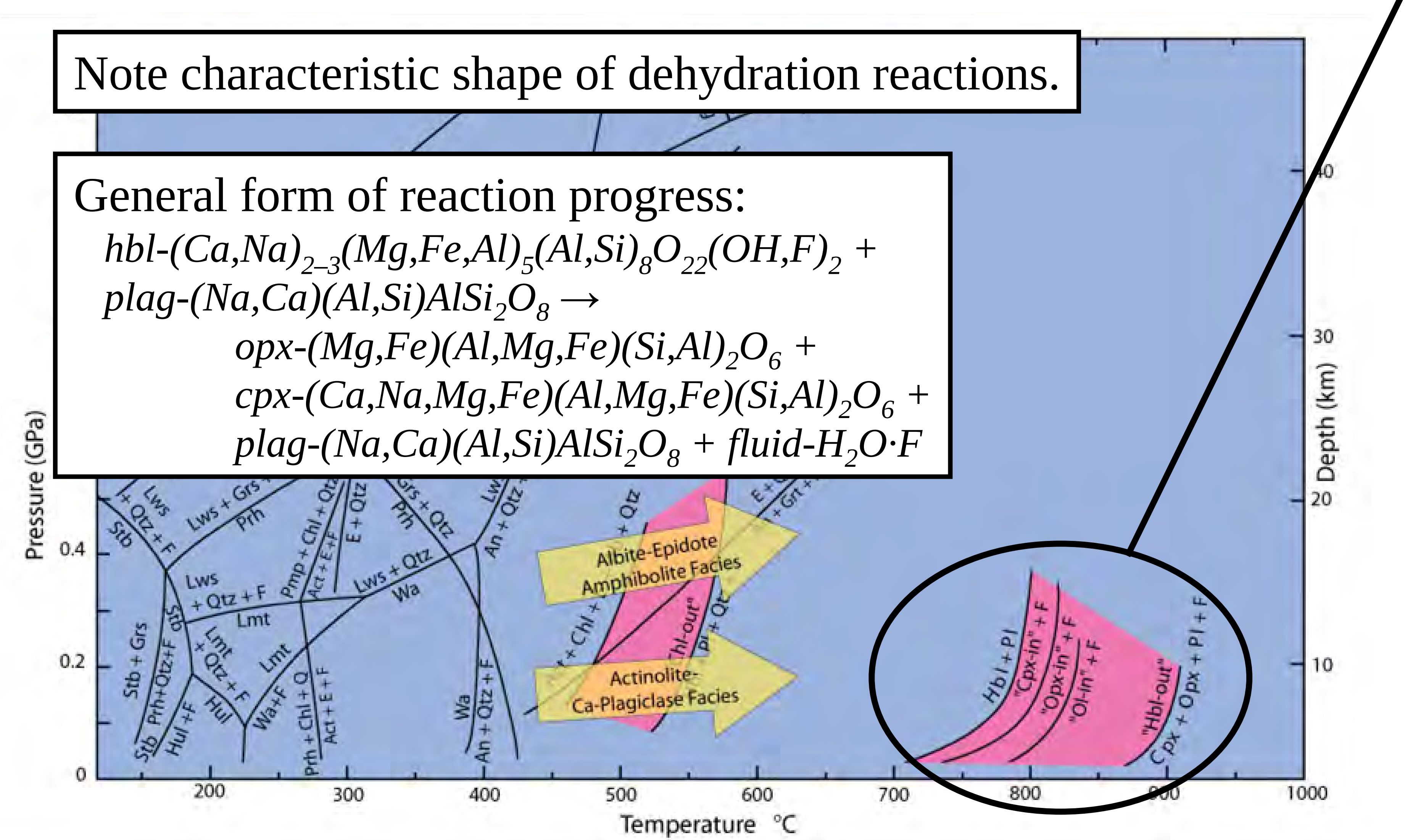


Fig. 26-19. Simplified petrogenetic grid for metamorphosed mafic rocks showing the location of several determined univariant reactions in the $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O\text{-}(Na_2O)$ system ("C(N)MASH"). Winter (2010) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

(C.Bina, 9/2011)

Dovolte mi, abych vám představil vaše nové nejlepší kamarády: minerály!

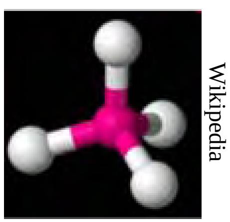
$\{MgO, FeO, SiO_2\}$

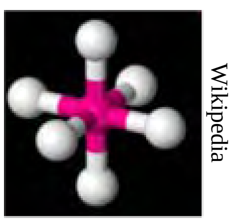
{hořčík, železo, křemen}

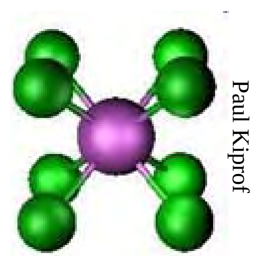
vic oxid křemičitý → ← *méně oxid křemičitý*

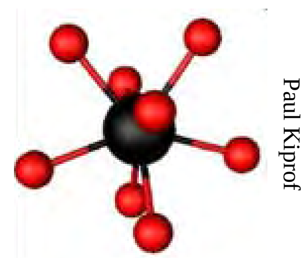
$(Mg,Fe)O$	$(Mg,Fe)_2SiO_4$	$(Mg,Fe)SiO_3$	SiO_2
magnesiowüstite	olivine	orthopyroxene	quartz *(křemen)*
nebo	$(Mg,Fe)^{VI}_2Si^{IV}O_4$	$(Mg,Fe)^{VI}Si^{IV}O_3$	$Si^{IV}O_2$
ferropericlase			
$(Mg,Fe)^{VI}O$			

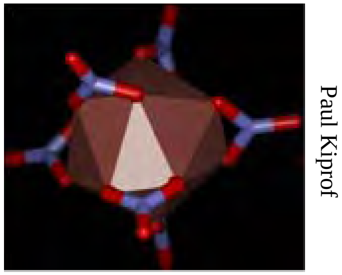
koordinační číslo











4-fold site (tetrahedral)	6-fold site (octahedral)	8-fold site (cubic)	8-fold site (dodecahedral)	12-fold site (icosahedral)

(C.Bina, 9/2011)

Dovolte mi, abych vám představil vaše nové nejlepší kamarády: minerály!

$\{MgO, FeO, SiO_2\}$

vic oxid křemičitý → ← *méně oxid křemičitý*

$(Mg,Fe)O$
magnesiowüstite
nebo
ferropericlase
$(Mg,Fe)^{VI}O$

pevný roztok s koncovými členy:

MgO = periclase

FeO = wüstite

John Betts Fine Minerals

$(Mg,Fe)_2SiO_4$
olivine
$(Mg,Fe)^{VI}{}_2Si^{IV}O_4$

pevný roztok s koncovými členy:

Mg_2SiO_4 = forsterite

Fe_2SiO_4 = fayalite

John Betts Fine Minerals

$(Mg,Fe)SiO_3$
orthopyroxene
$(Mg,Fe)^{VI}Si^{IV}O_3$

pevný roztok s koncovými členy:

$MgSiO_3$ = enstatite

$FeSiO_3$ = ferrosilite

John Betts Fine Minerals

SiO_2
quartz *(křemen)*
$Si^{IV}O_2$

John Betts Fine Minerals

solid solutions:

$$\mu_i = \mu_i^0 + T \cdot \mathbf{(nR \ln \gamma_i X_i)}$$

(entropy of mixing)

Complex solutions have expanded stability fields.

(C.Bina, 9/2011)

{MgO,FeO,SiO$_2$}

Vysoký tlak …

vic oxid křemičitý ⟶ $-\int \Delta S dT + \int \boldsymbol{\Delta V dP} = \Delta G < 0$ ⟵ *méně oxid křemičitý*

(Mg,Fe)O

magnesiowüstite

nebo

ferropericlase

(Mg,Fe)^{VI}O

John Betts Fine Minerals

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

vysoký tlak ↓

olivine

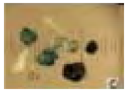
(Mg,Fe)$^{VI}_2$Si^{IV}O$_4$

Wikipedia

wadsleyite

(β-modified-spinel-type)

(Mg,Fe)$^{VI}_2$Si^{IV}O$_4$

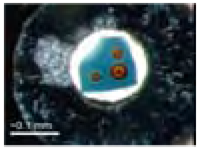


HACTO

ringwoodite

(γ-spinel-type)

(Mg,Fe)$^{VI}_2$Si^{IV}O$_4$



S.D.Jacobsen

(Mg,Fe)SiO$_3$

vysoký tlak ↓

orthopyroxene

(Mg,Fe)^{VI}Si^{IV}O$_3$

Wikipedia

akimotoite

(ilmenite-type)

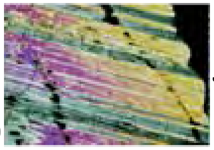
(Mg,Fe)^{VI}Si^{VI}O$_3$

N.Tomioka & K.Fujino

majorite

(garnet-type)

(Mg,Fe)$^{VIII}_3$[(Mg,Fe)^{VI}Si^{VI}]$_2$Si$^{IV}_3$O$_{12}$



J.Smyth

silicate perovskite

(CaTiO$_3$-type)

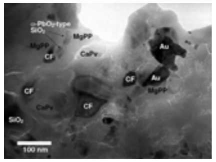
(Mg,Fe)^{VIII}Si^{VI}O$_3$

HACTO

post-perovskite

(CaIrO$_3$-type)

(Mg,Fe)^{VIII}Si^{VI}O$_3$



K.Hirose +

SiO$_2$

vysoký tlak ↓

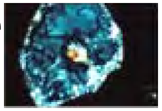
quartz

Si^{IV}O$_2$

Wikipedia

coesite

Si^{IV}O$_2$



J.Smyth

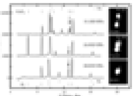
stishovite

Si^{VI}O$_2$

HACTO

CaCl$_2$-type

Si^{VI}O$_2$

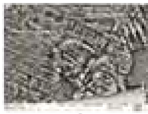


D. Lakshtanov +

seifertite

(α-PbO$_2$-type)

Si^{VI}O$_2$



BGI

(C.Bina, 9/2011)

{MgO,FeO,SiO_2,**CaO**}

Plus vápník …

$r_{Ca^{2+}} > r_{Mg^{2+}} \rightarrow V_{Ca} > V_{Mg}$

vic oxid křemičitý ⟶ ⟵ *méně oxid křemičitý*

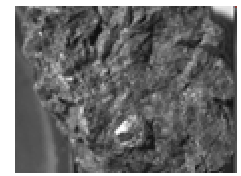
(Mg,Fe)O
magnesiowüstite
nebo
ferropericlase
$(Mg,Fe)^{VI}O$

$(Mg,Fe)_2SiO_4$
olivine
$(Mg,Fe)^{VI}{}_2Si^{IV}O_4$

$Ca(Mg,Fe)Si_2O_6$
clinopyroxene
$Ca^{VIII}(Mg,Fe)^{VI}Si^{IV}{}_2O_6$

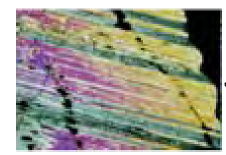
SiO_2
quartz
$Si^{IV}O_2$

vysoký tlak



Wikipedia

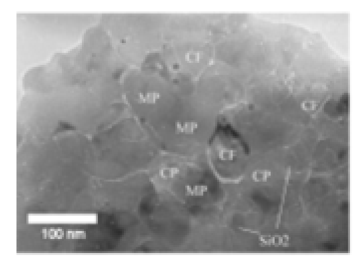
majorite
(garnet-type)



J.Smyth

$(Ca,Mg,Fe)^{VIII}{}_3[(Mg,Fe)^{VI}Si^{VI}]_2Si^{IV}{}_3O_{12}$

Ca-silicate perovskite
($CaTiO_3$-type)
$Ca^{XII}Si^{VI}O_3$



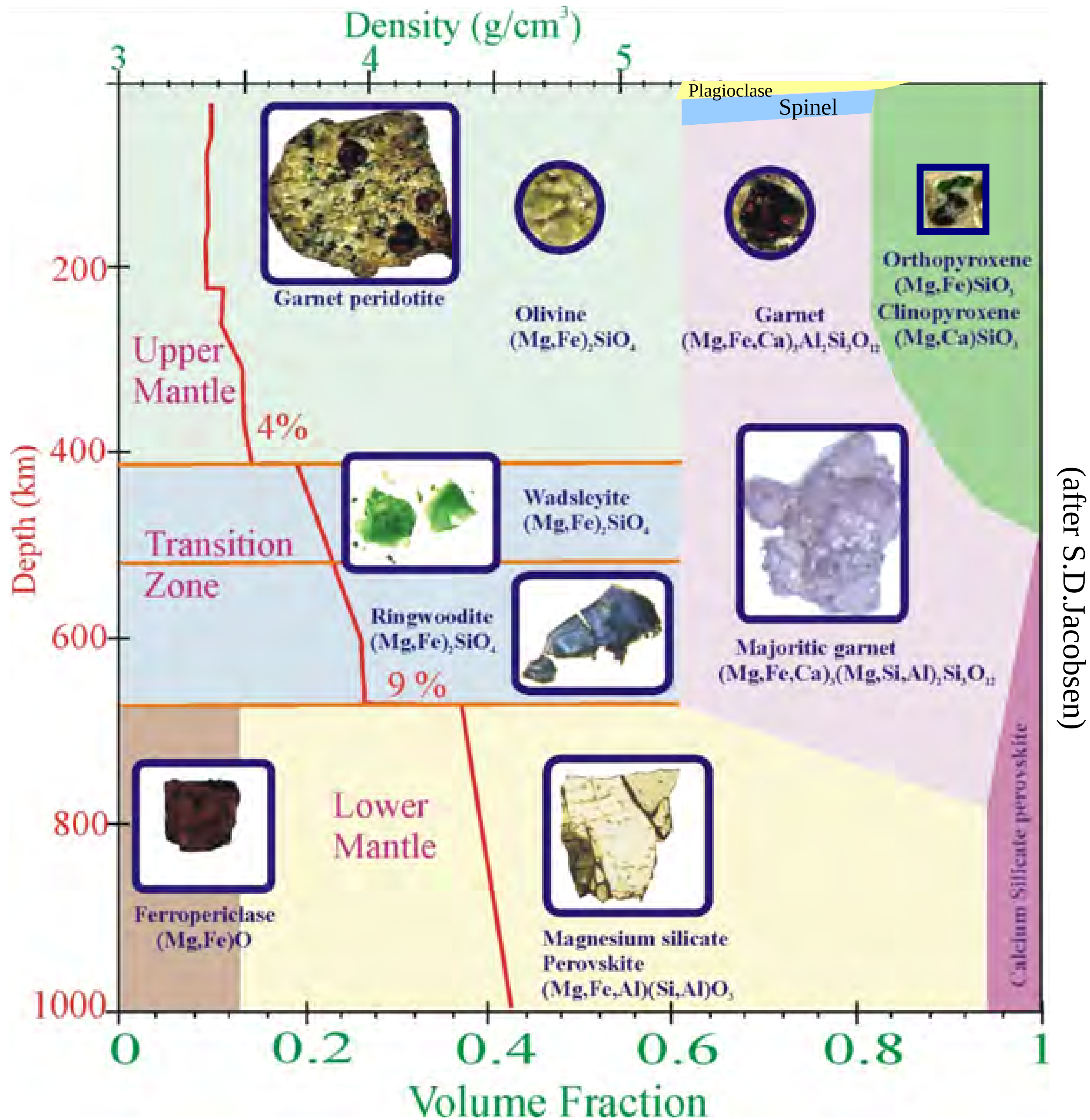
R.Sinmyo +

(C.Bina, 9/2011)

Introduction to Mantle Petrology

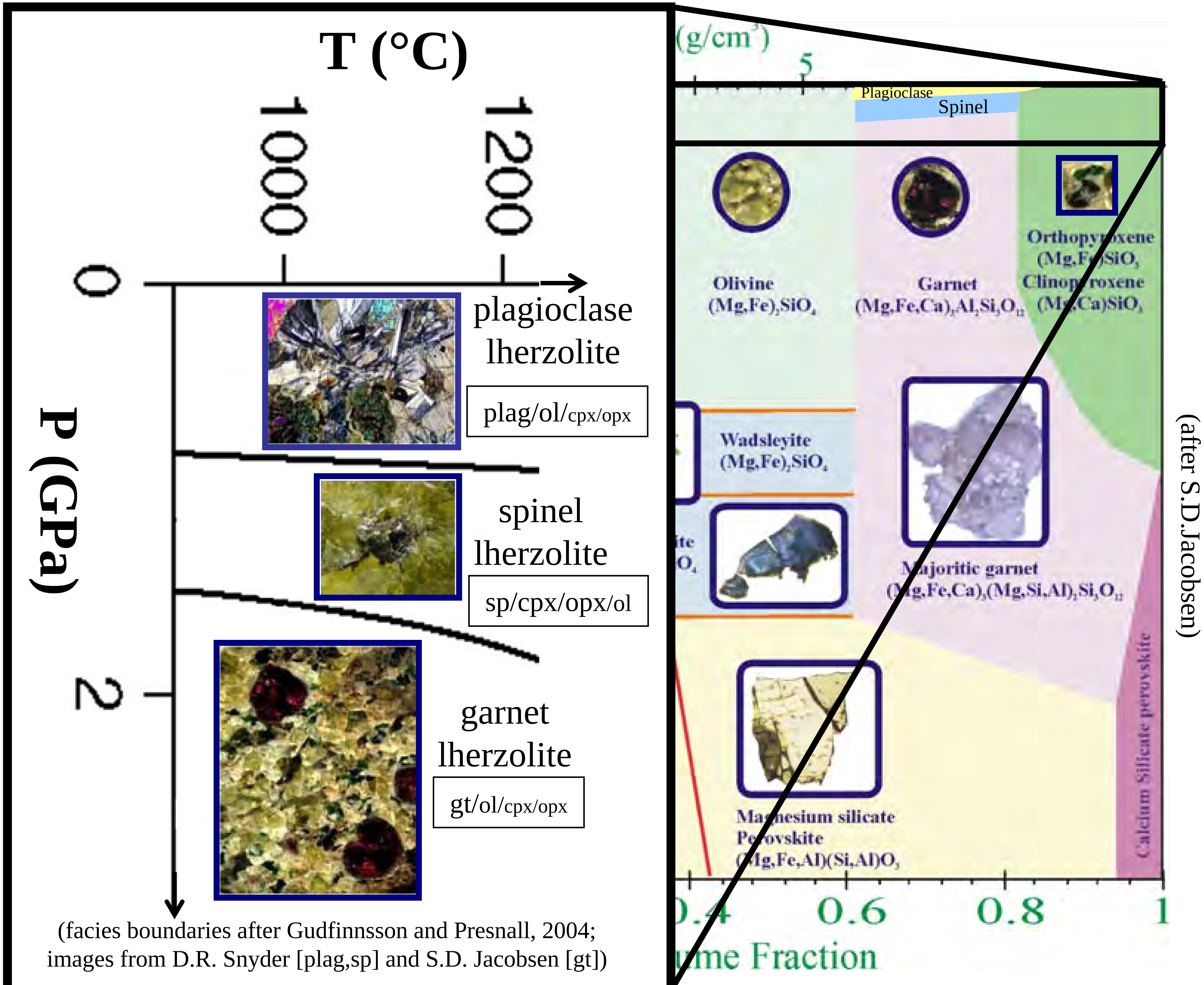
approximate depth limit of bulk xenolith samples

approximate depth limit of diamond inclusions



(C.Bina, 9/2011)

Introduction to Mantle Petrology



(C.Bina, 9/2011)

$\{MgO, FeO, CaO, SiO_2, \mathbf{Al_2O_3}\}$

A plus hliník …

Al^{3+}

$(Na,Ca)(Al,Si)AlSi_2O_8$

plagioclase *(sodnovápenatý živec)*

pevný roztok s koncovými členy:

$NaAlSi_3O_8$ = albite

$CaAl_2Si_2O_8$ = anorthite

Wikipedia

$Na^{V}(AlSi_3)^{IV}O_8$

$(Mg,Fe)Al_2O_4$

spinel *$(Mg,Fe)(Al,Cr)_2O_4$ …*

pevný roztok s koncovými členy:

$MgAl_2O_4$ = spinel

$FeAl_2O_4$ = hercynite

Wikipedia

$(MgAl)^{IV}Al^{VI}O_4$

$(Ca,Mg,Fe)_3(Al)_2Si_3O_{12}$

garnet *$(Ca,Mg,Fe,Mn)_3(Al,Fe^{3+},Cr)_2Si_3O_{12}$ …*

pevný roztok s koncovými členy:

$Mg_3Al_2Si_3O_{12}$ = pyrope

$Fe_3Al_2Si_3O_{12}$ = almandine

$Ca_3Al_2Si_3O_{12}$ = grossular

Wikipedia

$Fe^{VIII}{}_3Al^{VI}{}_2Si^{IV}{}_3O_{12}$

$(Mg,Fe)(Mg,Fe,Al)(Si,Al)_2O_6$

orthopyroxene

pevný roztok s koncovými členy:

$MgSiO_3$ = (ortho)enstatite

$FeSiO_3$ = (ortho)ferrosilite

$MgAl_2SiO_6$ = Mg-Tschermak's

Wikipedia

$Mg^{VI}Si^{IV}O_3$

$(Ca,Mg,Na)(Mg,Fe,Al)(Si,Al)_2O_6$

clinopyroxene

pevný roztok s koncovými členy:

$CaMgSi_2O_6$ = diopside

$CaFeSi_2O_6$ = hedenbergite

$CaAl_2SiO_6$ = Ca-Tschermak's

$MgSiO_3$ = clinoenstatite

$FeSiO_3$ = clinoferrosilite

$NaAlSi_2O_6$ = jadeite

Wikipedia

$Ca^{VIII}Mg^{VI}Si^{IV}{}_2O_6$

$(Mg,Fe,Ca,Na)(Al,Fe^{3+},Cr,Mg,Fe)(Si,Al,Fe^{3+})_2O_6$ …

(C.Bina, 9/2011)

Geobarometry and Geothermometry

PROBLEM:

How can we determine the pressure *or* temperature *of equilibration from the measured* compositions *of coexisting minerals?*

Geobarometry and Geothermometry

$$0 = \Delta G(P,T,X) = \Delta G^0(P,T) + RT \ln K_a$$

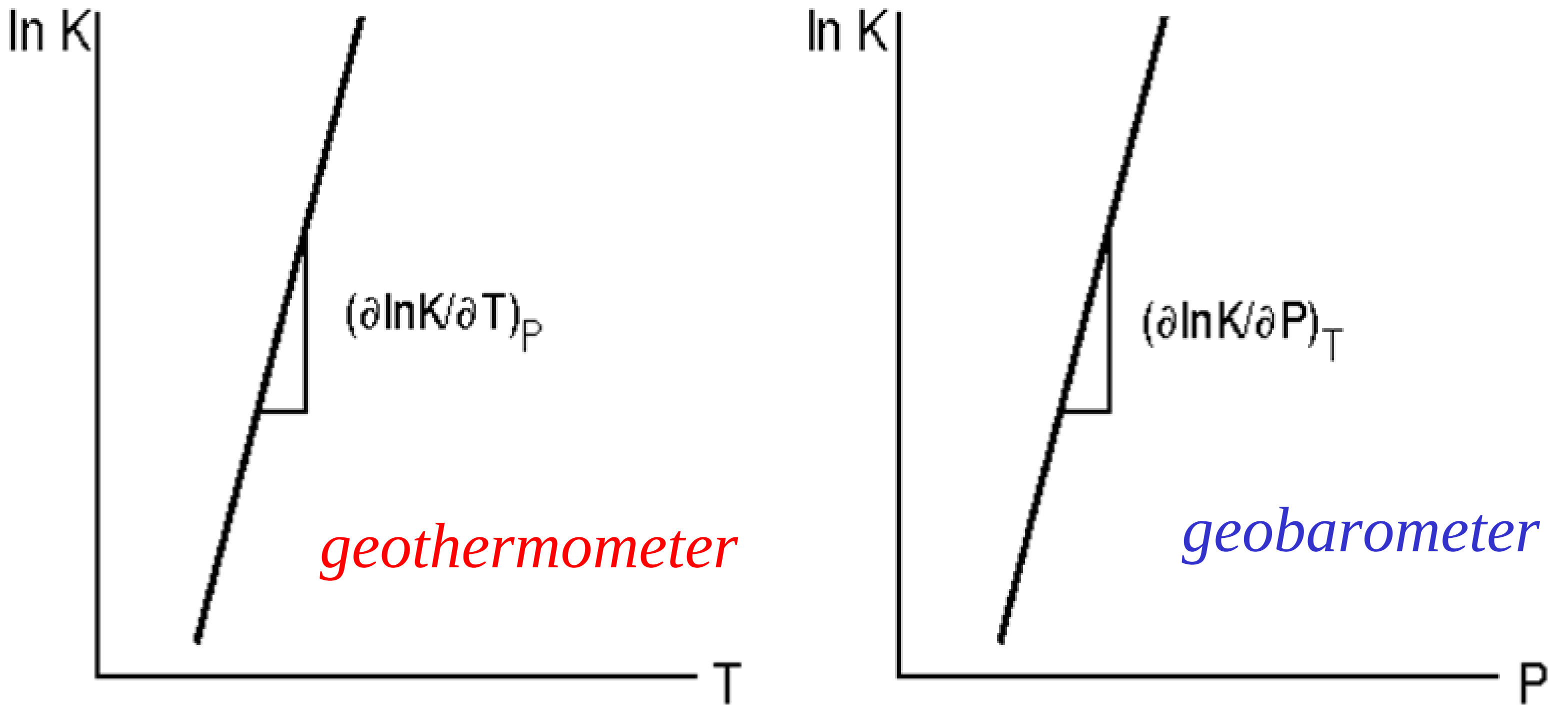
$$\boxed{\Delta G^0(P,T) = -RT \ln K_a}$$

Geobarometers: *composition* should be most sensitive to *pressure*: $|(\partial \ln K_a / \partial P)_T| >> |(\partial \ln K_a / \partial T)_P|$

Geothermometers: *composition* should be most sensitive to *temperature*: $|(\partial \ln K_a / \partial T)_P| >> |(\partial \ln K_a / \partial P)_T|$

(C.Bina, 9/2011)

Geobarometry and Geothermometry



Mineral equilibria that are used as geothermometers or geobarometers should have steep slopes in *ln K vs. T* (left) and *ln K vs. P* (right) diagrams, respectively. Errors in *ln K* lead only to small errors in the estimated temperatures and pressures if this is the case.

(Figure 21b of Will, 1998)

Geobarometry and Geothermometry

Geothermometers: *composition* should be most sensitive to *temperature*: $|(\partial \ln K_a / \partial T)_P| >> |(\partial \ln K_a / \partial P)_T|$

Thus, they should have large ΔS (or ΔH) relative to ΔV.

(prostá kationtová záměna)

Typically: a cation-exchange reaction (*e.g.*, Mg^{2+}-Fe^{2+}, Mn^{2+}-Fe^{2+}, Ni^{2+}-Mg^{2+}) involving little volume change.

For example, the "*Fe-Mg* garnet-clinopyroxene geothermometer":

$$Fe_3Al_2Si_3O_{12} + 3\ CaMgSi_2O_6 \leftrightarrow Mg_3Al_2Si_3O_{12} + 3\ CaFeSi_2O_6$$

almandine (gt) | diopside (cpx) | pyrope (gt) | hedenbergite (cpx)

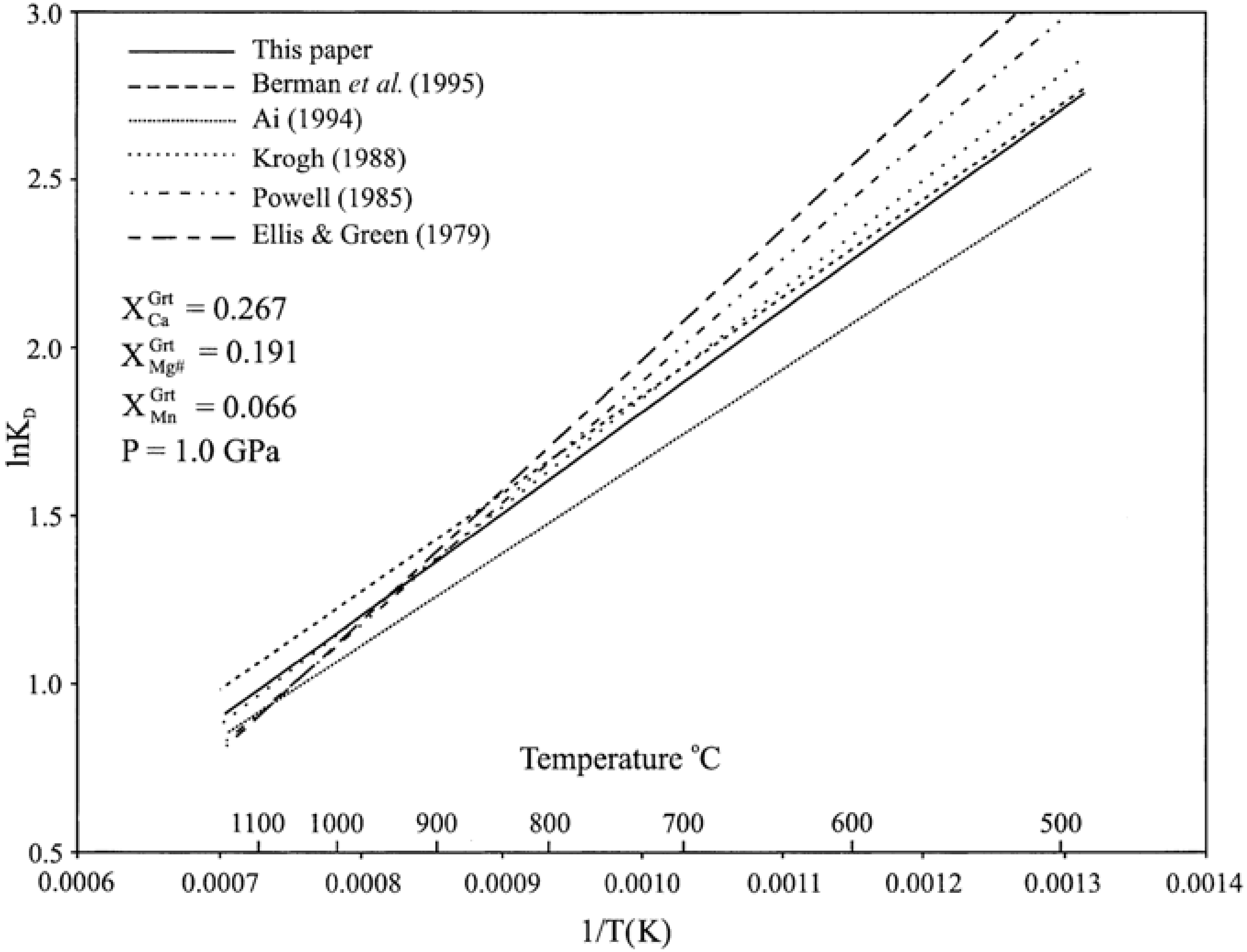
find compositions of coexisting *gt*-$(Mg,Fe)_3Al_2Si_3O_{12}$ and *cpx*-$Ca(Mg,Fe)Si_2O_6$

(granát) *(klinopyroxen)*

(cf. Will, 1998; Ravna, 2000)

(C.Bina, 9/2011)

Geobarometry and Geothermometry



$$K = \frac{\left(a^{gt}_{Mg_3Al_2Si_3O_{12}}\right)\left(a^{cpx}_{CaFeSi_2O_6}\right)}{\left(a^{gt}_{Fe_3Al_2Si_3O_{12}}\right)\left(a^{cpx}_{CaMgSi_2O_6}\right)}$$

***Fe-Mg* garnet-clinopyroxene geothermometer**

Plot of *ln* K_D versus *1/T* at 1.0 GPa for various versions of the garnet–clinopyroxene Fe^{2+}–Mg thermometer, calculated for the garnet composition given in Table 4. K_D has been varied by changing the Fe^{2+}/Mg ratio of the clinopyroxene.

(Figure 3 of Ravna, 2000)

(C.Bina, 9/2011)

Geobarometry and Geothermometry

Geobarometers: *composition* should be most sensitive to *pressure*: $|(\partial \ln K_a / \partial P)_T| >> |(\partial \ln K_a / \partial T)_P|$

Thus, they should have large ΔV relative to ΔS (or ΔH).

Typically: a mass-transfer reaction involving a change in coordination number (and thus a volume change).

For example, the "*GASP* geobarometer":

$$2\ Al_2^{VI}SiO_5 + Ca_3Al_2^{VI}Si_3O_{12} + SiO_2 \leftrightarrow 3\ CaAl_2^{IV}Si_2O_8$$

kyanite — grossular (gt) — quartz — anorthite (plag)

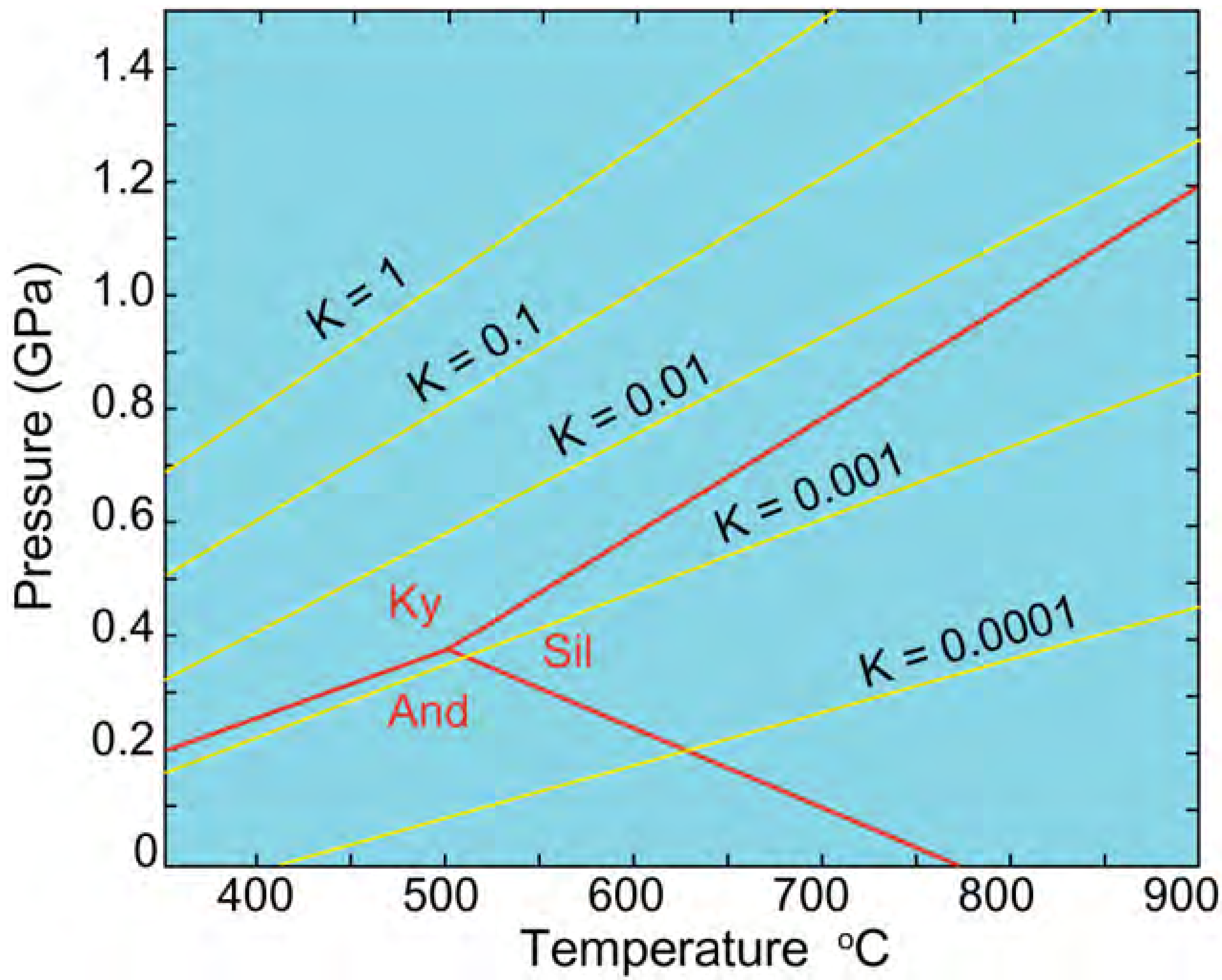
GASP = "**G**rossular-**A**luminosilicate-***S****i*O_2-**P**lagioclase"

measure coexisting *gt*-$(Ca,Mg,Fe)_3(Al)_2Si_3O_{12}$ and *plag*-$(Na,Ca)(Al,Si)AlSi_2O_8$

(granát) (cf. Will, 1998; Holdaway, 2001) *(sodnovápenatý živec)*

(C.Bina, 9/2011)

Geobarometry and Geothermometry



$$K = \frac{\left(a^{gt}_{Ca_3Al_2Si_3O_{12}}\right)}{\left(a^{plag}_{CaAl_2Si_2O_8}\right)^3}$$

***GASP* geobarometer**

(Figure 27.98 of Spear, 1993)

(C.Bina, 9/2011)

Let's Examine Some Example Transitions in Detail

čedič *eklogit* *gabro* *eklogit*

The "Basalt → Eclogite" or "Gabbro → Eclogite" Transition

(cf. Wood, 1987; Gubbins et al, 1994; Helffrich, 1996; Hacker, 1996)

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sodnovápenatý živec *spinel* *granát* *lherzolit*

The Plagioclase → Spinel → Garnet Lherzolite Transitions

(cf. O'Neill, 1981; Wood and Yuen, 1983; Carroll Webb and Wood, 1996; Nickel, 1986; Robinson and Wood, 1998)

The "Basalt → Eclogite" or "Gabbro → Eclogite" Transition

Facies: granulite → garnet granulite → eclogite [→ coesite eclogite]

Reactions:

orthopyroxene + clinopyroxene + plagioclase → garnet + quartz

orthopyroxene + plagioclase → garnet + quartz

plagioclase → clinopyroxene + quartz

Example: 1.55 $Mg_2Si_2O_6$ (opx) + $CaAl_2Si_2O_8$ (plag) →

0.85 $Mg_3Al_2Si_3O_{12}$ (gt) + 0.15 $Ca_3Al_2Si_3O_{12}$ (gt) +

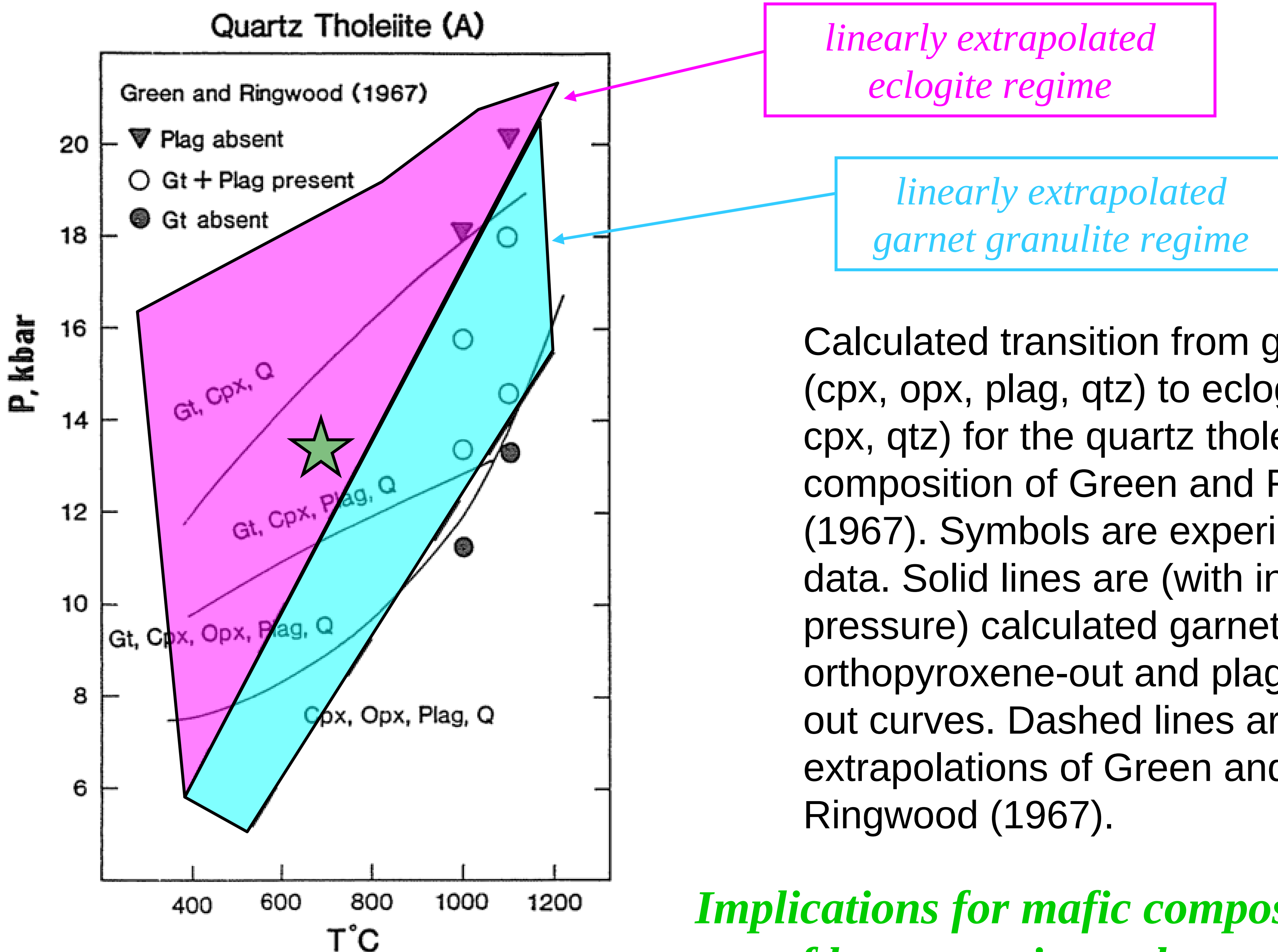
0.55 $CaMgSi_2O_6$ (cpx) + SiO_2 (qtz)

Summary: gt increases; opx vanishes; plag decreases and vanishes

[Later: SiO_2 (qtz)→SiO_2 (coes)]

(C.Bina, 9/2011)

gabbro → eclogite transition



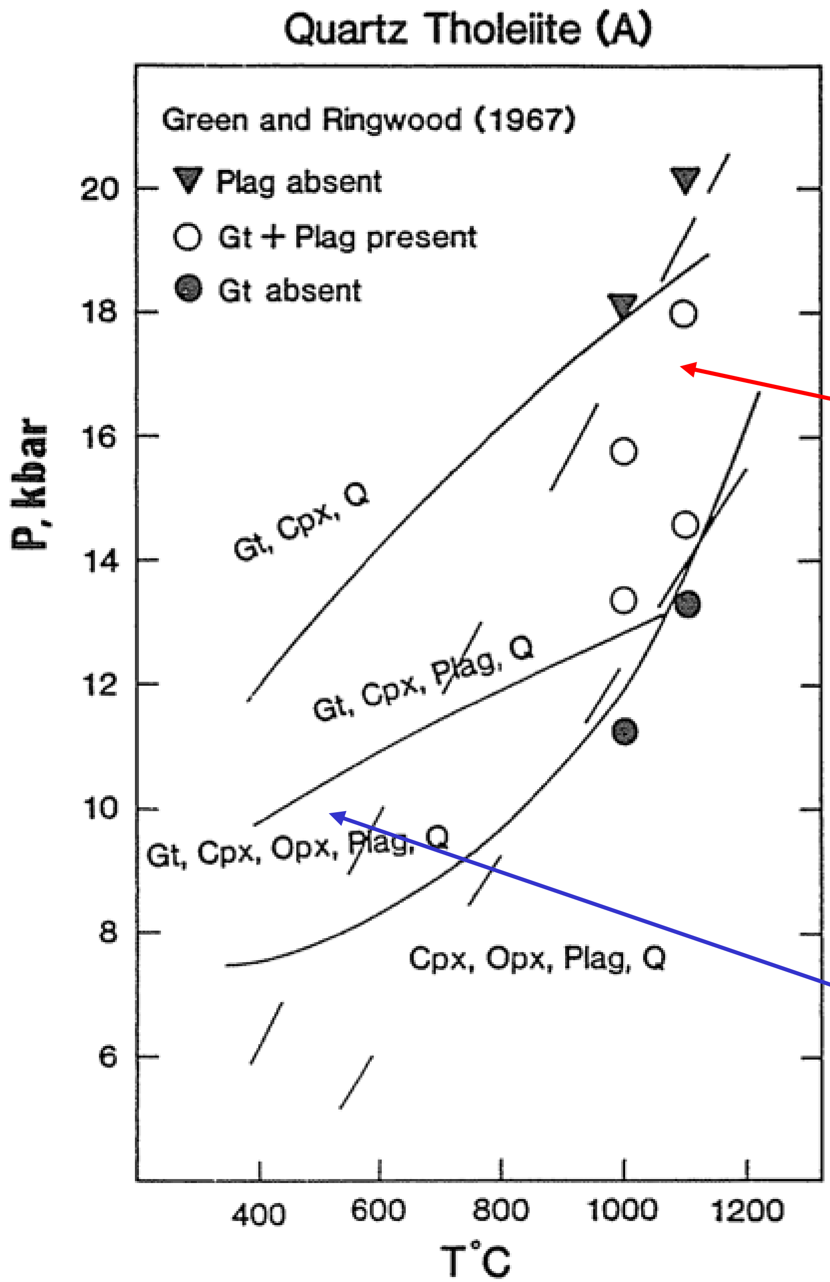
(Figure 3 of Wood, 1987)

Calculated transition from gabbro (cpx, opx, plag, qtz) to eclogite (gt, cpx, qtz) for the quartz tholeiite (A) composition of Green and Ringwood (1967). Symbols are experimental data. Solid lines are (with increasing pressure) calculated garnet-in, orthopyroxene-out and plagioclase-out curves. Dashed lines are extrapolations of Green and Ringwood (1967).

Implications for mafic composition of lower continental crust?

(C.Bina, 9/2011)

gabbro → eclogite transition



(Figure 3 of Wood, 1987)

Actual phase boundaries are curved!

Pyroxenes and garnets are solid solutions at high temperatures:

$Mg(Mg,Al)(Si,Al)_2O_6$ opx (En + Ts)

$(Ca,Mg)(Mg,Al)(Si,Al)_2O_6$ cpx (Di + Ts + cEn)

$(Mg,Ca)_3Al_2Si_3O_{12}$ gt (Pyr + Gro)

Garnet stability field expands at low temperatures, as pyroxenes become nearly pure phases while garnet remains a solid solution:

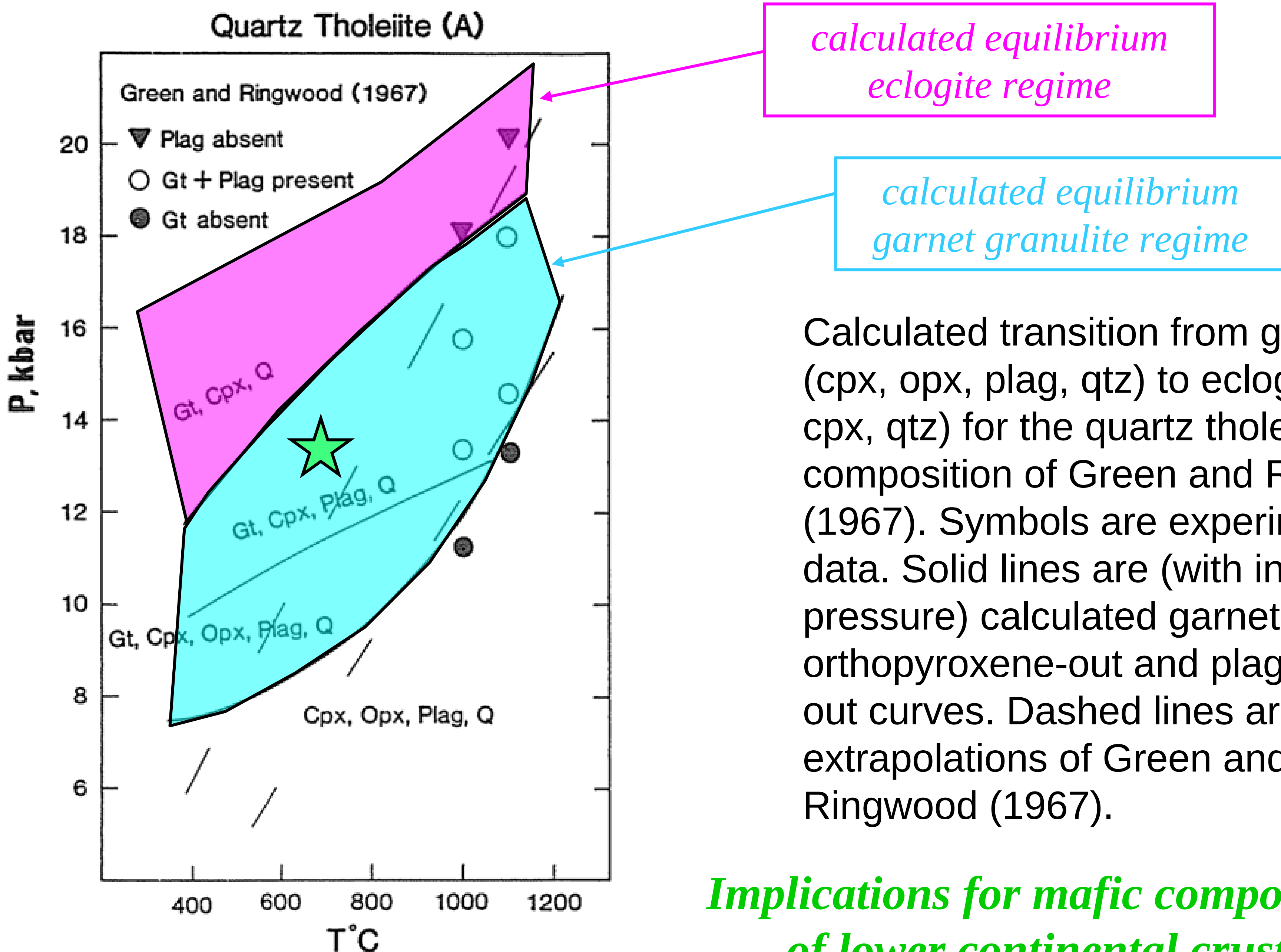
$Mg(Mg)(Si)_2O_6$ opx (En)

$(Ca)(Mg)(Si)_2O_6$ cpx (Di)

$(Mg,Ca)_3Al_2Si_3O_{12}$ gt (Pyr + Gro)

(C.Bina, 9/2011)

gabbro → eclogite transition



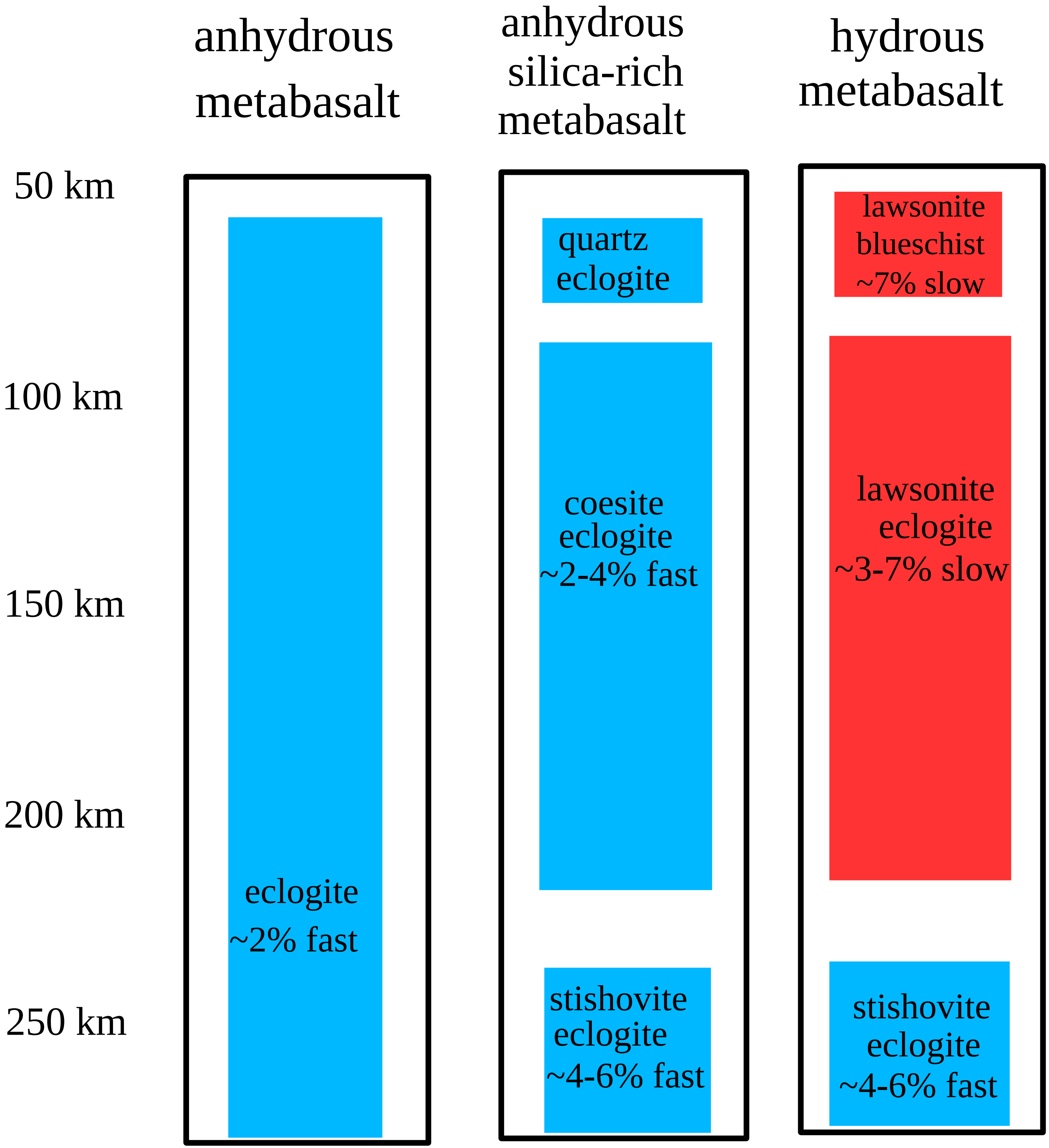
(Figure 3 of Wood, 1987)

Calculated transition from gabbro (cpx, opx, plag, qtz) to eclogite (gt, cpx, qtz) for the quartz tholeiite (A) composition of Green and Ringwood (1967). Symbols are experimental data. Solid lines are (with increasing pressure) calculated garnet-in, orthopyroxene-out and plagioclase-out curves. Dashed lines are extrapolations of Green and Ringwood (1967).

Implications for mafic composition of lower continental crust?

(C.Bina, 9/2011)

gabbro → eclogite transition



Implications for seismic velocity structure of subducting oceanic crust?

Helffrich et al., 1989
Helffrich & Stein, 1993
Peacock, 1993
Hacker, 1996
Helffrich, 1996
Connolly & Kerrick, 2002
Bina, 2003

(C.Bina, 9/2011)

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: $CaAl_2Si_2O_8$ (plag) + 2 Mg_2SiO_4 (olv) →

$MgAl_2O_4$ (sp) + $Mg_2Si_2O_6$ (opx) + $CaMgSi_2O_6$ (cpx)

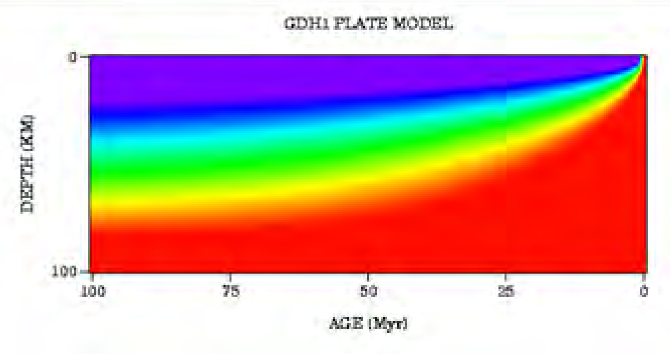
Example 2: $MgAl_2O_4$ (sp) + 1.55 $Mg_2Si_2O_6$ (opx) + 0.45 $CaMgSi_2O_6$ (cpx)

→ 0.85 $Mg_3Al_2Si_3O_{12}$ (gt) + 0.15 $Ca_3Al_2Si_3O_{12}$ (gt) + Mg_2SiO_4 (olv)

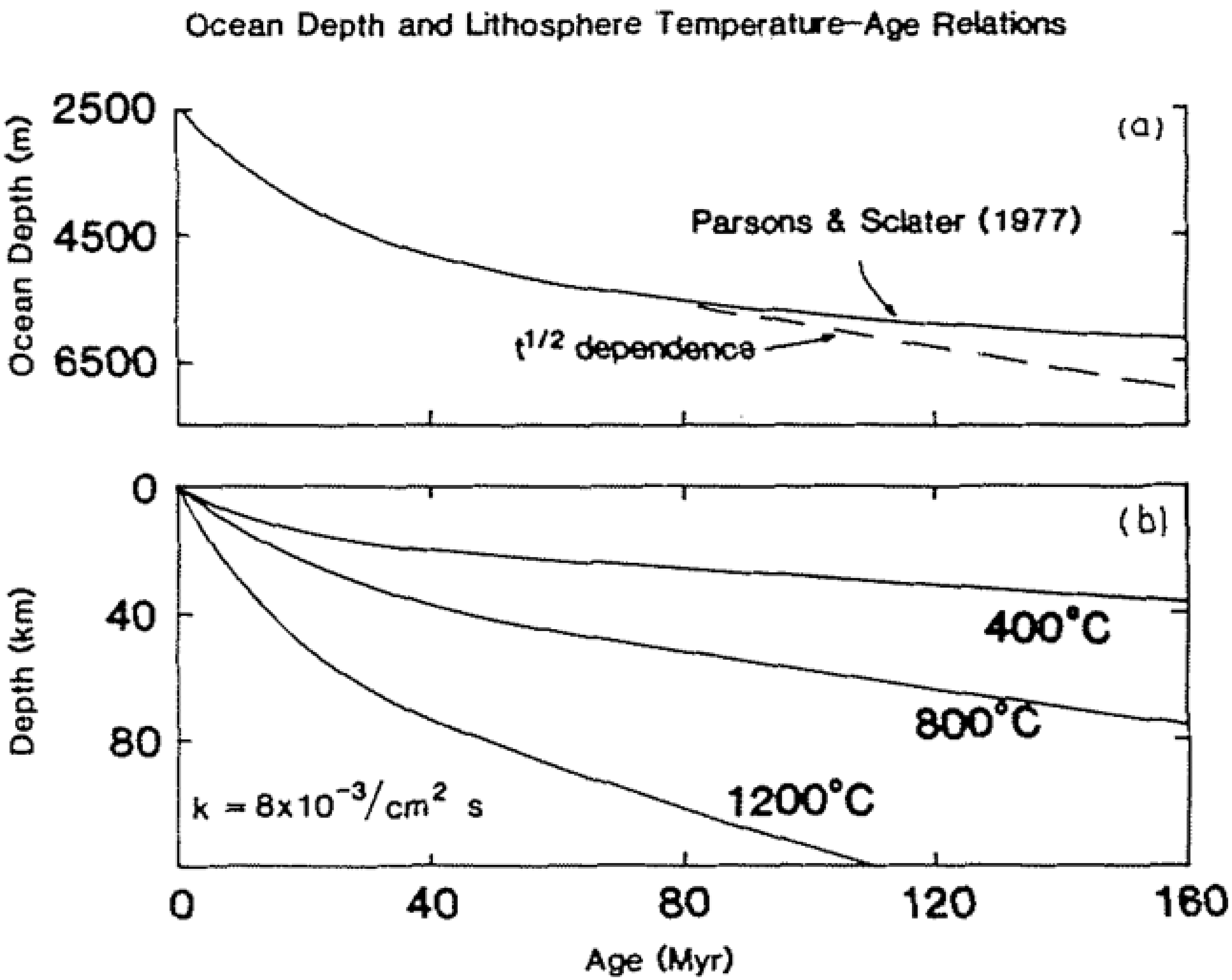
Summary 1: sp, opx and cpx increase; plag vanishes; olv decreases

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

plagioclase → spinel → garnet lherzolite transitions



(after Stein and Stein, 1992)

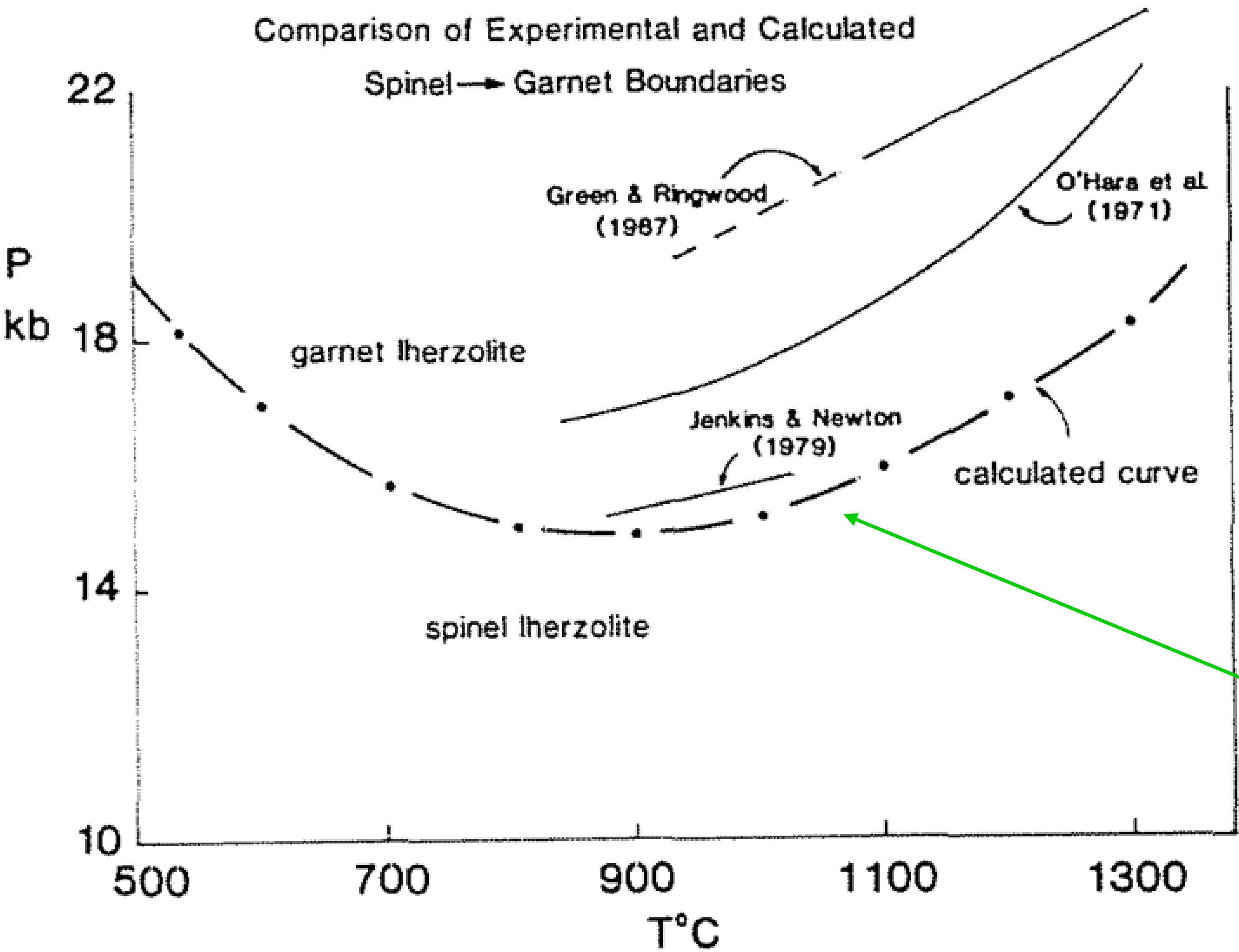


(a) Comparison of observed ocean depths with those predicted for a conductively cooled plate ($t^{1/2}$ curve). (b) Temperature-depth profiles for pure conductive cooling (equation (1)) with thermal diffusivity of 8×10^{-3} cm^2/s and maximum temperature of 1350°C.

(Figure 1 of Wood and Yuen, 1983)

(C.Bina, 9/2011)

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)

(C.Bina, 9/2011)

spinel → garnet lherzolite transition

Increasing pressure: $\Delta V<0$

At very low temperatures:

$MgAl_2O_4 + 1.55\ Mg_2Si_2O_6 + 0.45\ CaMgSi_2O_6$

spinel   enstatite (opx)   diopside (cpx)

↓ (increasing P)

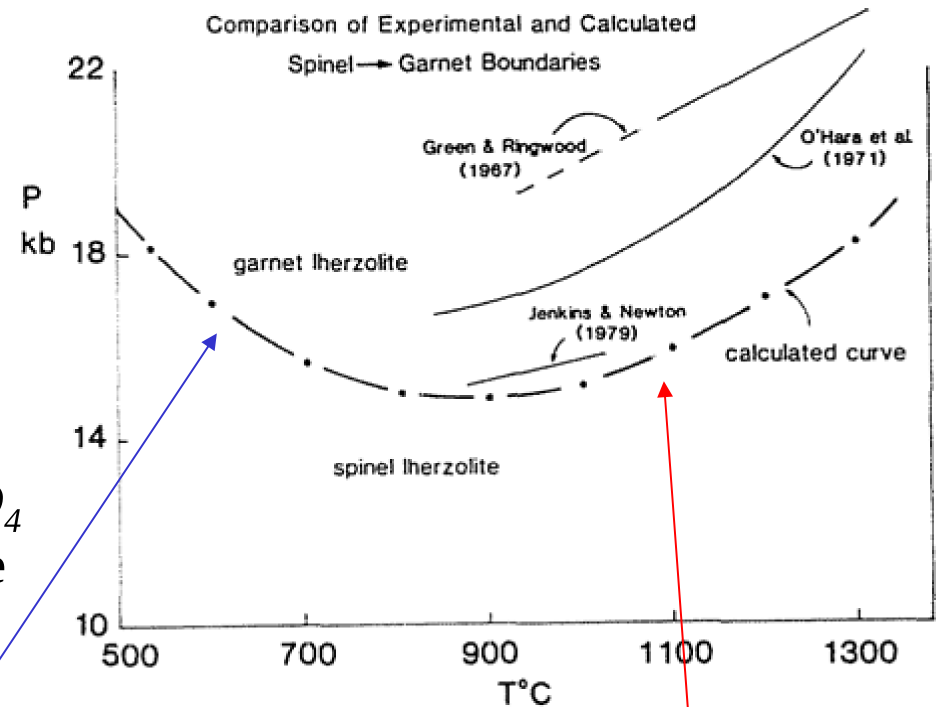
$0.85\ Mg_3Al_2Si_3O_{12} + 0.15\ Ca_3Al_2Si_3O_{12} + Mg_2SiO_4$

garnet solid solution (pyrope + grossular)   olivine

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

$(Mg_{0.85}Ca_{0.15})_3Al_2Si_3O_{12}$

$\Delta S>0$



(Figure 3 of Wood and Yuen, 1983)

At higher temperatures:

Reactants become solid solutions, too:

$\Delta S<0$

$Mg(Mg,Al)(Si,Al)_2O_6$ $(Ca,Mg)(Mg,Al)(Si,Al)_2O_6$

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

(C.Bina, 9/2011)