# Exercises

*1. Clapeyron slope - general features.* Although the indicated chemical reactions (below) are highly schematic, they must in principle be balanced. Subscripts $_R$ and $_P$ indicate reactants and products, respectively. A reaction written as e.g. Solids$_R$ = Solids$_P$, might have one, or more than one, phase on each side.

a. Relate dT, dp, $\Delta$S and $\Delta$V by the Clapeyron equation (write the equation. Develop the Clapeyron equation (mathematically) from the expression for $\Delta G = \Delta E + p\Delta V + T\Delta S$, based on the andalusite to kyanite transition example in the figure, below.
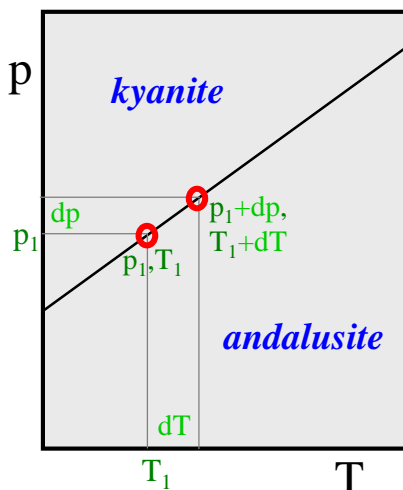
**Clayperon-equation**

$$dp\Delta V = dT\Delta S$$
$$dp/dT = \Delta S/\Delta V$$

$$\Delta G = \Delta E + p_1\Delta V - T_1\Delta S = 0$$
$$\Delta G = \Delta E + (p_1+dp)\Delta V - (T_1+dT)\Delta S = 0$$

Subtracting the upper from the lower equation

⬇

$$dp\Delta V - dT\Delta S = 0$$
$$dp\Delta V = dT\Delta S$$
$$dp/dT = \Delta S/\Delta V$$



b. State or discuss the signs (positive or negative) for $\Delta$S and $\Delta$V of the schematic reactions 1-3 (below). Discuss specifically why $\Delta$V is likely to change more than $\Delta$S with increasing pressure in reactions 2 and 3.

1. Reaction occurring in response to **increasing p**: Solids$_R$ = Solids$_P$

   Always: $\Delta V < 0$

   Commonly $\Delta$S is also negative, but sometimes the high-presure phase(s) has/have higher entropy than the the reacting low-low pressure phases
   (e.g. $S_{sillimanite} > S_{andalusite}$ and $S_{bridgmanite} > S_{akimotoite}$).

2. Melting reaction: Solids$_R$ = Melt$_P$

   Always: $\Delta S > 0$

   Normally $\Delta$V is also positive, but melts are more compressible than solids, leading to steadily decreasing $\Delta$V with increasing p within the stability range of a certain subsolidus mineral assemblage. Exceptionally, this may lead to negative $\Delta$V and an associated melt-solid density cross-over.

3. Devolatilisation reactions: Solids$_R$ = Solids$_P$ + fliud/vapour
   e.g. $KAl_2Si_3AlO_{10}(OH)_2$(muscovite) + $SiO_2$(quartz) = $KAlSi_3O_8$(K-felspar) + $Al_3SiO_5$(kynaite) + $H_2O$(vapour)
   or: $CaCO_3$(calcite) + $SiO_2$(quartz) = $CaSiO_3$(wollastonite) + $CO_2$(vapour)

   Always: $\Delta S > 0$

   $\Delta$V is positive at low pressure, but fluids are very compressible, leading to steadily decreasing $\Delta$V with increasing p within the stability range of a certain subsolidus mineral assemblage. Exceptionally, this may lead to negative $\Delta$V and an associated fluid-solid density cross-over.

**2. Phase relations in the MgSiO₃ system**. *The phases with compositions **other than MgSiO₃** are listed in the grey box.* The phase fields are marked with phase names, as well as abbreviations (bold letters).

a. Why do the melting curves have more curvature (with the convex side towards the melt field) than the majority of the solid-solid phase transitions?

Melts are generally more compressible than coexisting solids. Because $\Delta S$ of a melting reaction (solid → melt) is always positive and changes relatively little with pressure, the Clapeyron slope $dp/dT = \Delta S/\Delta V$ will increase with increasing p as $\Delta V$ decreases (for the most common situation of $\Delta V>0$). If $\Delta V$ reaches 0 and turns negative the melting curve will "curve around" and attain a negative dp/dT slope.

b. Which of the two phases **LT-cpx** and **opx** is **most** compressible? **opx** (same explanation as above)

c. Which of the two phases **mj** and **bm** has the the **largest** molar volume? **mj** (because mj is the **low-p** phase)

d. Which of the phases **ak** and **bm** has the **largest** molar volume? **ak** (because ak is the **low-p** phase)

e. Use the Clapeyron relation to deduce the phase in each of the following two pairs with the **largest** entropy?

**mj** or **bm**: **mj**      **ak** or **bm**: **bm**      Explain briefly your reasoning:

If you have wrong answers in c and d, you should get **bm** and **ak**, respectively.
The reactions **mj**→**bm** and **ak**→**bm** have $\Delta V < 0$ (3c-d, because they occur in response to increasing p at constant T).
The phase diagram shows that the first reaction has $dp/dT = \Delta S/\Delta V > 0$ and that the second reaction has $dp/dT= \Delta S/\Delta V < 0$. The reactions **mj**→**bm** and **ak**→**bm** have therefore negative and positive $\Delta S$, respectively.

f. Use the phase rule to find the variance (F) at the points a, b, c and d and along the phase boundaries a-b and c-d. For each of the six cases you should **specify** the components (C) and phases (P) - **not just** their numbers.

**Note**: For a valid phase rule analysis of variance, the univariant phase boundaries (e.g. a-b) **cannot not include** invariant end points, like a and b.

**a**: C: 2: MgO, SiO₂
   P: 4: wd, rw, st, ak
   F: 4–4 = 0, invariant

**b**: C: 2: MgO, SiO₂
   P: 4: wd, st, ak, mj
   F: 4–4 = 0, invariant

**a-b**: C: 2: MgO, SiO₂
   P: 3: wd, st, ak
   F: 4–3 = 1, univariant

**c**: C: 1: MgSiO₃
   P: 3: mj, ak, bm
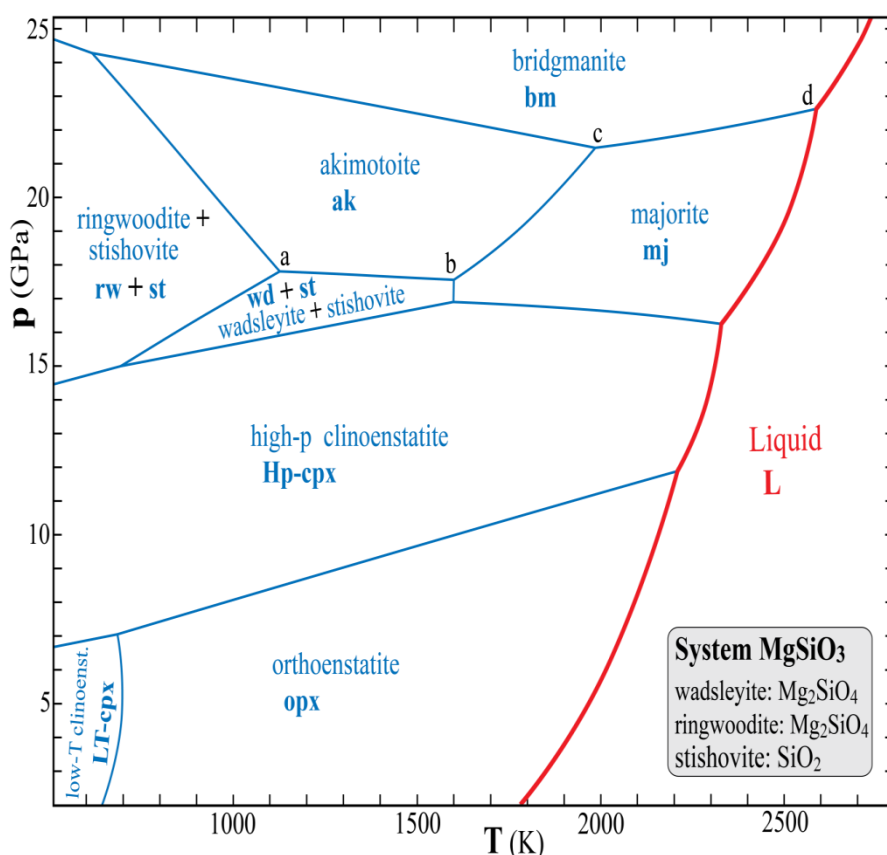   F: 3–3 = 0, invariant

**d**: C: 1: MgSiO₃
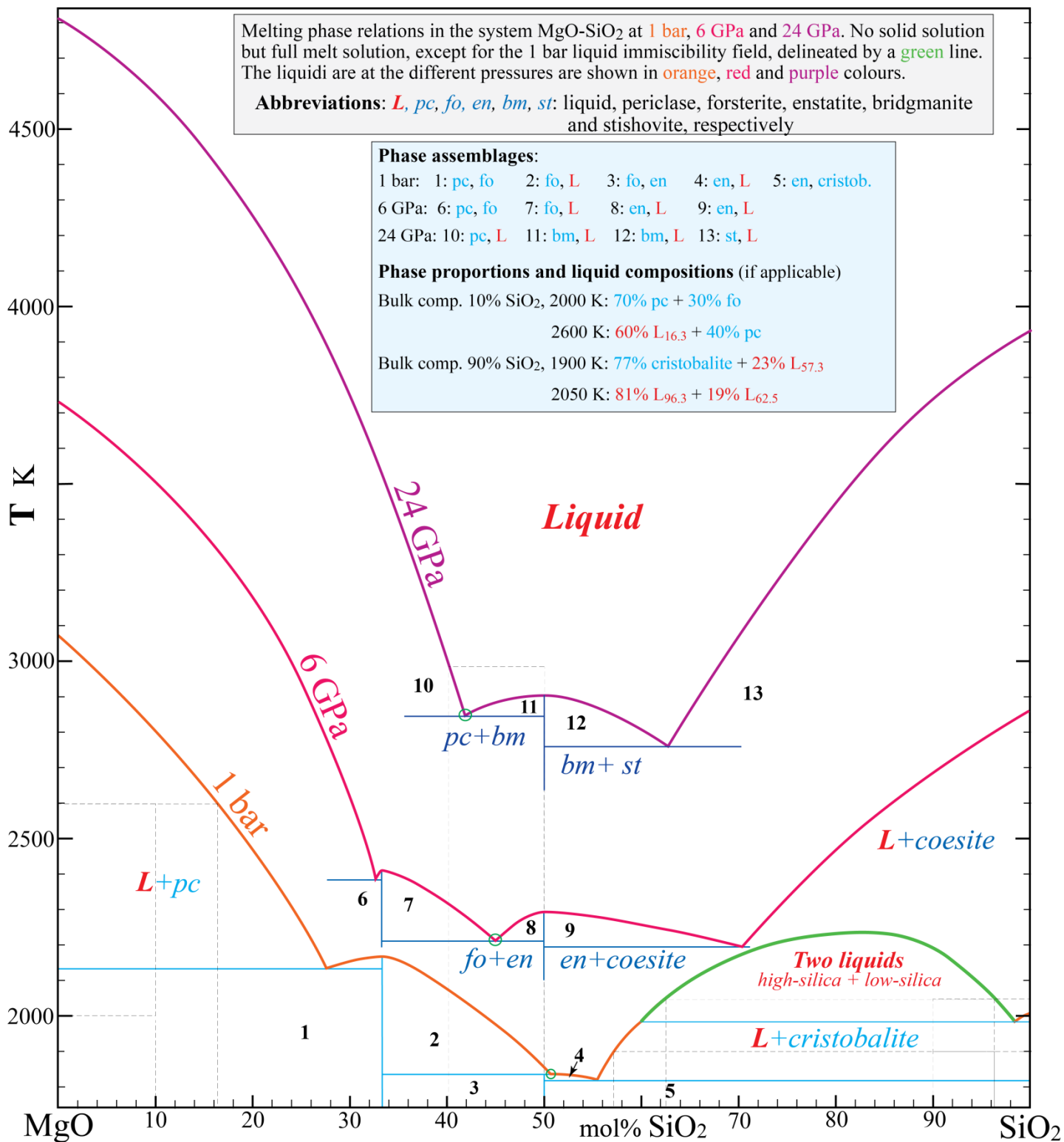   P: 3: mj, bm, L
   F: 3–3 = 0, invariant

**c-d**: C: 1: MgSiO₃
   P: 2: mj, bm
   F: 3–2 = 1, univariant



P (GPa) vs T (K) phase diagram for the System MgSiO₃. Labelled phase fields: bridgmanite (bm), akimotoite (ak), majorite (mj), ringwoodite + stishovite (rw + st), wadsleyite + stishovite (wd + st), high-p clinoenstatite (Hp-cpx), orthoenstatite (opx), low-T clinoenst. (LT-cpx), Liquid (L). Points a, b, c, d marked.

System MgSiO₃
wadsleyite: Mg₂SiO₄
ringwoodite: Mg₂SiO₄
stishovite: SiO₂

# 3. Melting phase relations in the system MgO-SiO₂ - *se further descriptions in the grey box.*

a. Give the phase assemblages (without phase proportions and compositions, use the abbreviations) for the numbered field in the light blue box.

b. Give (blue box) the phase proportions and liquid compositions (if applicable) for bulk compositions with 10 and 90% $SiO_2$ at the indicated temperatures. You can give the liquid compositions as $L_X$, where X is mol% $SiO_2$.

c. Assume that a typical peridotite in this simple model system has 60% olivine and 40% orthopyroxene. Give the approximate model composition in mol% $SiO_2$ of such a peridotite: **40 mol%**

d. Mark the initial (invariant) melt compositions of such a model peridotite at 1 bar, 6 GPa and 24 GPa with small rings.

e. How does the invariant melt compositions of a peridotite in this system change with increasing pressure from 1 bar to 24 GPa? **The melt composition becomes more magnesian.**



Melting phase relations in the system MgO-SiO₂ at 1 bar, 6 GPa and 24 GPa. No solid solution but full melt solution, except for the 1 bar liquid immiscibility field, delineated by a green line. The liquidi are at the different pressures are shown in orange, red and purple colours.

**Abbreviations**: *L, pc, fo, en, bm, st*: liquid, periclase, forsterite, enstatite, bridgmanite and stishovite, respectively

**Phase assemblages**:
1 bar:  1: pc, fo    2: fo, L    3: fo, en    4: en, L    5: en, cristob.
6 GPa:  6: pc, fo    7: fo, L    8: en, L    9: en, L
24 GPa: 10: pc, L    11: bm, L    12: bm, L    13: st, L

**Phase proportions and liquid compositions** (if applicable)
Bulk comp. 10% SiO₂, 2000 K: 70% pc + 30% fo
                          2600 K: 60% L₁₆.₃ + 40% pc
Bulk comp. 90% SiO₂, 1900 K: 77% cristobalite + 23% L₅₇.₃
                          2050 K: 81% L₉₆.₃ + 19% L₆₂.₅

4. *General features of melting curves, exemplified by an* **imaginary one-component system** *with three solid phases* α, β *and* γ. *The left figure panel shows the molar volume V for melt and solids (along the melting curve) as a function of pressure.*

Melting reactions (solid → liquid) have positive heat of fusion (subscript m for melting), $\Delta H_m = \Delta E + p\Delta V_m > 0$. The relation $\Delta G_m = \Delta H_m - T\Delta S_m = 0$ at equilibrium (at the melting curve) **requires** that $\Delta S_m > 0$. Make the simplifying assumption that $\Delta S_m$ is **constant** in the problem below.

a. Draw $\Delta V_m$ as a function of pressure in the middle panel, using the same relative scale for the $\Delta V_m$-panel as for the V-panel and your mm-ruler for measurements.

b. Draw the complete p-T phase diagram in the right panel. Put the melting curve-segments through the four fixed points marked by red circles at pressures of 30, 50, 100 and 125 GPa. The α-β and β-γ phase transitions should have Clapeyron slopes (dp/dT) of −5.0 and +6.7 MPa/K, respectively. **Label the four phase fields**.



V
relative scale

$0 \quad \Delta V_m$
same scale as for V,
a 0-line is indicated

T °K
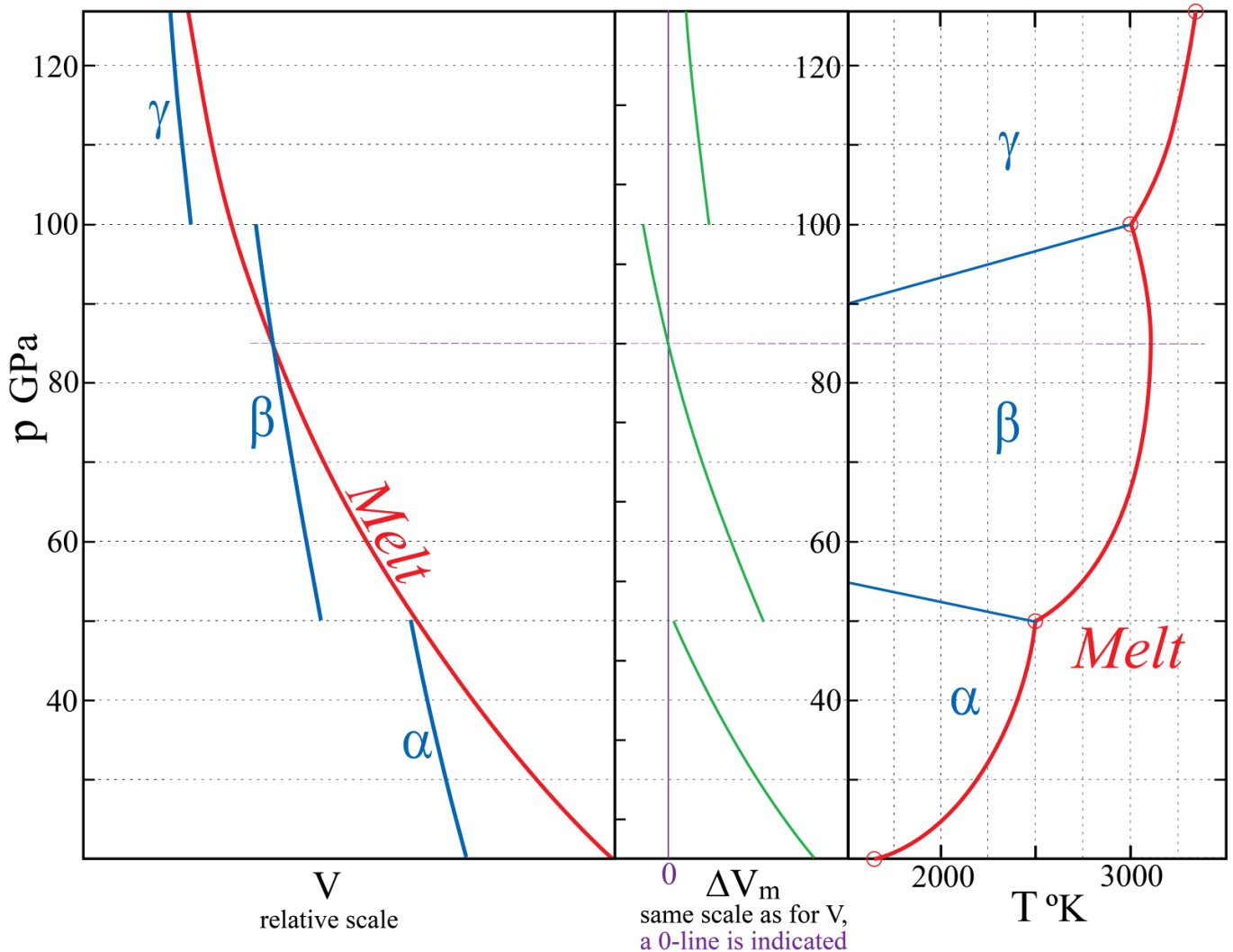
*c.* Explain briefly why pT-melting curves are almost always convex towards the liquid field?
Because the melt is more compressible than the solids, which results in decreasing $\Delta V_m$ and therefore increasing dp/dT = $\Delta S_m/\Delta V_m$ with increasing p for each melting curve segment, representing one specific subsolidus assemblage

d. $\Delta V_m$ for very high pressure partial melting of multi-component peridotite is likely to become negative within certain depth intervals in the Earth's mantle. The preferential partitioning of Fe into melt will contribute to such a density crossover. During early Earth differentiation, late-stage melts from mantle magma ocean crystallisation and partial melts formed in very hot mantle plumes, rising from the core-mantle boundary, were therefore likely to accumulate at two different depth levels in the the Earth.
Give the two levels: **410 km** (or slightly deeper) and the **core-mantle boundary**. I will also give 50% points for Moho, although that melt accumulation level is relevant for **basaltic**, rather than **peridotitic** melts.
and the corresponding depth ranges (very approximate) where peridotitic melt would sink (be negatively buoyant):
300-410 km and approximately lower 500-1000 km of the mantle.
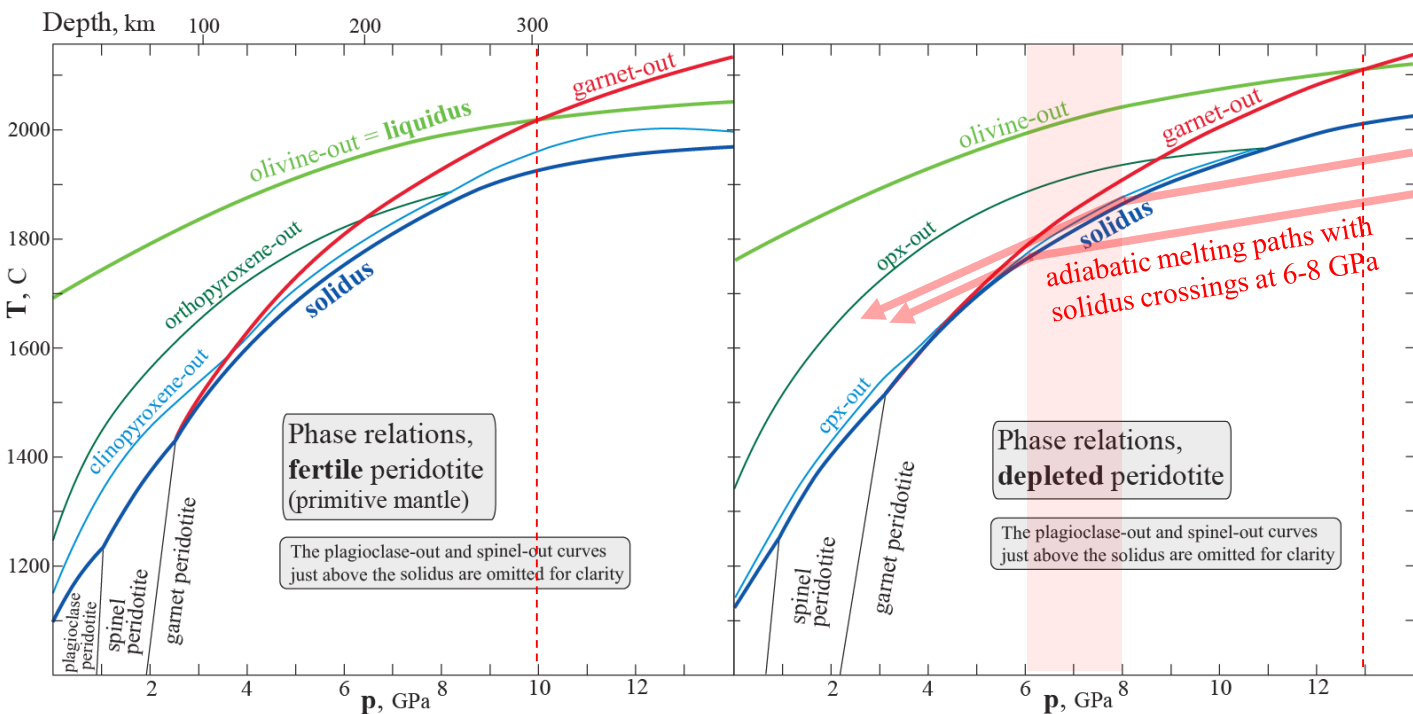
## 5. Melting phase relations of fertile and depleted peridotite compositions.

a. Write the **balanced** chemical reactions for the following two subsolidus transitions:

   1) plagioclase to spinel lherzolite in the system: $CaO-MgO-AlO_{1.5}-SiO_2$

   $$CaAl_2Si_2O_8 + 2\ Mg_2SiO_4 = MgAl_2O_4 + CaMgSi_2O_6 + 2\ MgSiO_3$$

   2) spinel to garnet lherzolite in the system: $MgO-AlO_{1.5}-SiO_2$

   $$MgAl_2O_4 + 4\ MgSiO_3 = Mg_3Al_2Si_3O_{12} + Mg_2SiO_4$$

b. Based on the suprasolidus phase relations above, show the following **approximate** compositions  (with correct relative positions) in the $CaO-AlO_{1.5}$-  and $NaO_{0.5}-MgO$-diagrams below (relative scale, only).  Use small rings around the numbers, 1-4.  A fertile lherzolite composition is indicated in both of the diagrams with a cross.
   1. Low-degree melt formed near the solidus
   2. Melt formed by more extensive melting
   3. Residue from the low-degree melting
   4. Residue from the extensive melting

c. What is the **two-phase mineralogy** and rock name for extensively melt-depleted residues at $p < 6\text{-}8$ GPa ?
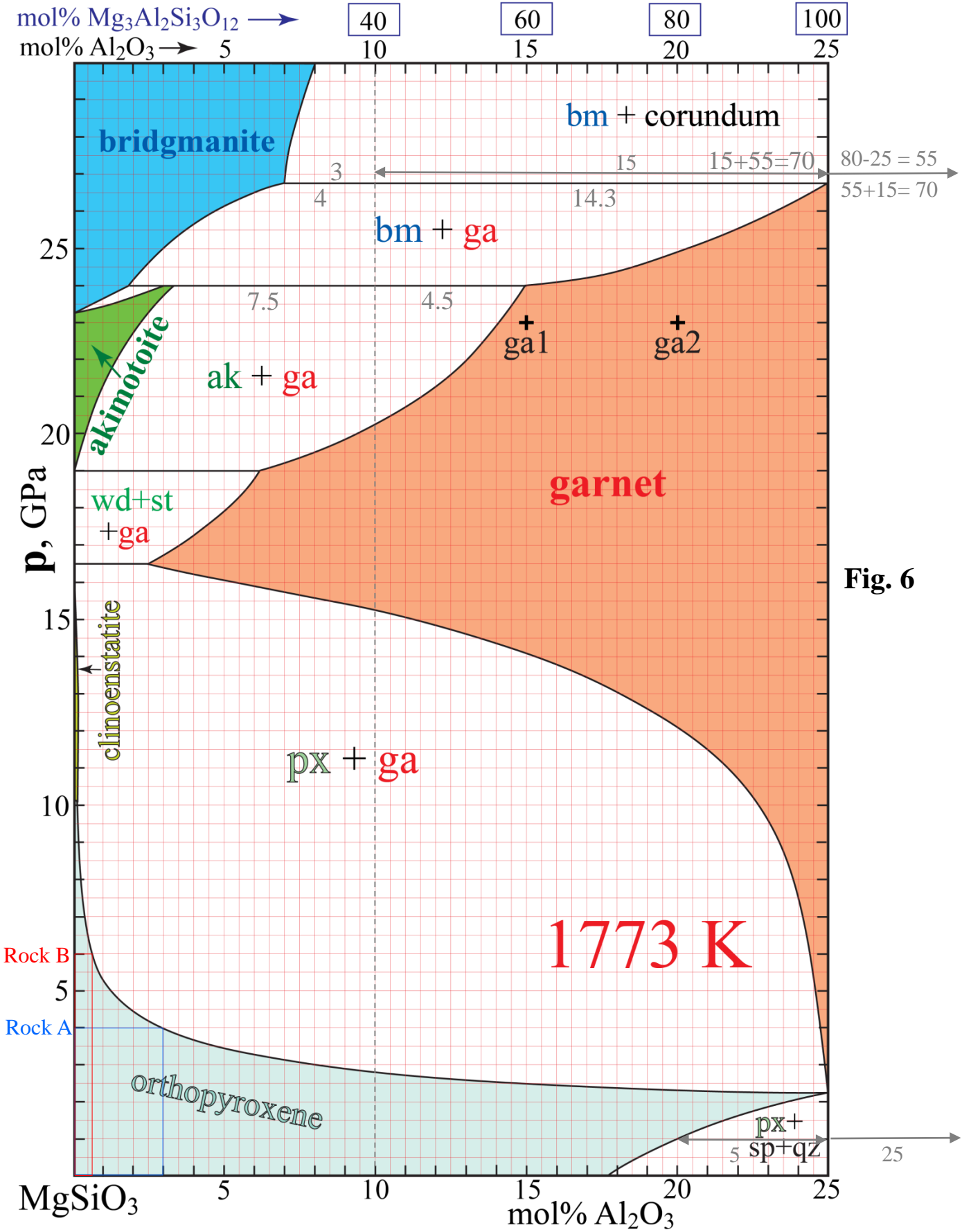   (Note that melting will stop well before p=0)
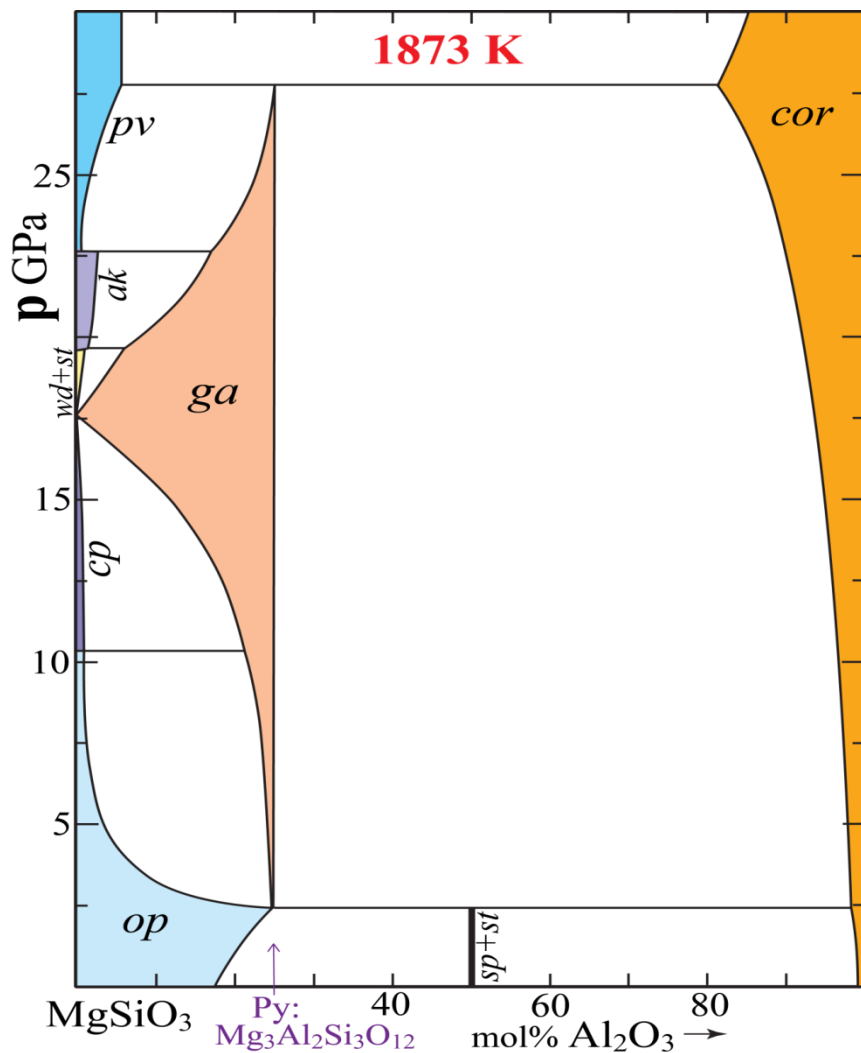
   The two main minerals: <u>ol + opx</u>    Rock name: <u>harzburgite.</u>
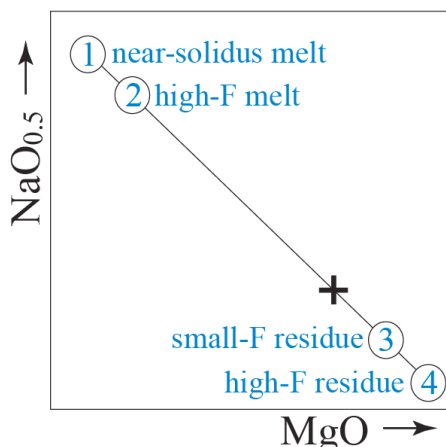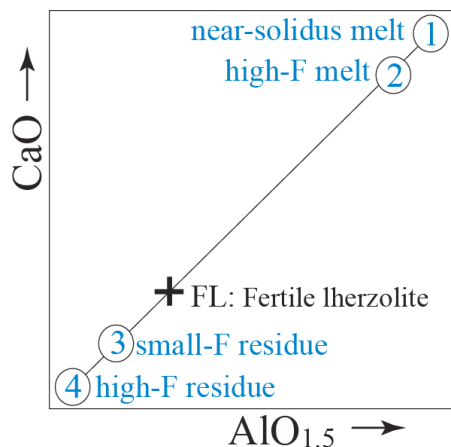


Because the minor minerals clinopyroxene and the Al-rich phases, containing high Ca, Na (+most incompatible trace elem.) and Al (from the Al-rich phases) contribute most to the early melt fractions

**6. The system MgSiO₃-Al₂O₃ at 1773 K and 5-30 GPa**. **The small figure on the next page shows the entire system.**
Abbreviations and compositions: px, sp, qz, st, ga, wd, ak, bm and co: pyroxene, spinel (stoichiometric $MgAl_2O_4$), quartz and stishivite (both stoichiometric $SiO_2$), garnet, wadsleyite (stoichiometric $Mg_2SiO_4$), akimotoite, bridgmanite and corundum (at 27 GPa: **80 mol% Al₂O₃, co₈₀**), respectively.



Fig. 6

**1873 K** ... p GPa ... *pv*, *cor*, *ak*, *wd+st*, *ga*, *cp*, *op*, *sp+st* ... MgSiO₃ ... Py: Mg₃Al₂Si₃O₁₂ ... mol% Al₂O₃ →

a. The generalized garnet formula is $A_3B_2C_3O_{12}$, where A, B and C are three distinct cation types. Give the cation valence and coordination numbers of O around the cation sites corresponding to the A, B and C cation sites.

**A-site:** valence: **2+** coord.: **8**   **B-site:** valence: **3+** and majorite 2+ & 4+ coord.: **6**   **C-site:** valence: **4+** coord.: **4**

b. Explain briefly why garnet has 25 mol% $Al_2O_3$ as an **upper** limit, based on a simple crystallographic consideration.
   The $Al^{3+}$ ions are only accepted into the octahedral (B) site, corresponding to 25% $Al_2O_3$ and 75% $MgSiO_3$

c. Give values for mol% pyrope in the four empty boxes along the top compositional axis.

d. Give the the exact amount of Al, Si and Mg atoms per formula unit **in the B-site** of the two majoritic garnet compositions g1 and g2 shown in the phase diagram. The sum of the B-site atoms must be 2.
   **g1**: Al: **1.2**  Si: **0.4**  Mg: **0.4**         **g2**: Al: **1.6**   Si: **0.2**   Mg: **0.2**

e. Give the compositions and proportions (%) of the equilibrium phases for a bulk composition of 10 % $Al_2O_3$
   (abbreviated: **bc₁₀**) at 1773 K and the given pressures. Use numbers rounded off to one decimal. You should give the phase (mineral) compositions as mol% $Al_2O_3$ as subscripts to the phase abbreviation (e.g. **px₂₀**).
   Assume that the solid solution range for corundum at 27 GPa is **co₈₀** at 27 GPa

   20.0 GPa: **100% ga₁₀**              23.5 GPa: **62.5% ga₁₄.₅ + 37.5% ak₂.₈**

   26.5 GPa: **78.1% bm₆.₀ + 21.9% ga₂₄.₃**      27.0 GPa: **95.9% bm₇.₀ + 4.1% co₈₀**

f. At 1 GPa, the assemblage spinel+quarts (i.e. $MgAl_2O_4+SiO_2$) lies outside /to the right of) the phase diagram.

   Give mol% $Al_2O_3$ for this pure assemblage on the $MgSiO_3$-$Al_2O_3$ join: **50**  and the mol ratio of sp/qz: **1**.
   We are on the $MgSiO_3$-$Al_2O_3$ join, where the spinel-quartz asseblage $MgAl_2O_4+SiO_2$ corresponds to
   1 mol $MgSiO_3$ + 1 mol $Al_2O_3$, i.e. to 50 mol% $MgSiO_3$ + 50 mol% $Al_2O_3$

   Give the compositions and proportions (%) of pyroxene and the combined sp+qz assemblage for for a bulk
      composition of 25% $Al_2O_3$ (**bc₁₀**):    **83.3%  px₂₀ + 16.7% (sp-qz)₅₀**

g. Specify the actual **components, C** and **phases, P,** (***not*** only the numbers of components and phases), and use the phase rule to investigate the variance (F) for the following bulk compositions (**bc**, with mol% $Al_2O_3$ as subscript) and pressures:

In the range $bc_{4\text{-}10}$ and **4-15 GPa**

C: $MgSiO_3 + Al_2O_3$ **or** $MgSiO_3 + Mg_3Al_2Si_3O_{12}$

P: px + ga

F= 3 − 2 = 1, univariant

In the range $bc_{10\text{-}25}$ and **16-20 GPa**

C: $MgSiO_3 + Al_2O_3$ **or** $MgSiO_3 + Mg_3Al_2Si_3O_{12}$

P: ga

F= 3 − 1 = 2, divariant

At $bc_0$ and **16.5 GPa**

C: $MgO + SiO_2$

P: px + wd + st

F= 3 − 3 = 0, invariant

At $bc_0$ and **19.0 GPa**

C: $MgO + SiO_2$

P: ak + wd + st

F= 3 − 3 = 0, invariant

h. What is the direct (and easy) indication of the presence of a majorite component in a complex garnet formula ?
   Si > 3.00 in a formula normalized to a sum of 12 oxygen atoms or 8 cations

i. Calculate the proportions of the garnet end member components andradite, grossular, spessartine, almandine, pyrope
   and majorite ($Mg_4Si_4O_{12}$) in the garnet compositions below. Not all of the composition contain all of the components.
   For the allocation of cations to the components, follow the order: andr, gros, spes, alm, pyr, maj (as the sequence above).
   If there is too little  Ca for andradite, try to allocate the rest of the $Fe^{3+}$ to the skiagite component: $Fe^{2+}_3 Fe^{3+}_2 Si_3O_{12}$.
Andradite from $Fe^{3+}$ (if too litte Ca: calculate skiagite from remaining $Fe^{3+}$),  grossular from the rest of Ca,  spessartin from
Mn,  almandine from (remaining) $Fe^{2+}$,  pyrope from remaining Al and majorite  from remaining Mg and Si.

Comment:  Alternatively, one could calculate skiagite first from all the $Fe^{3+}$ in the mineral formulas.  For the three garnet compositions used
here, that would be possible and it would result in no andradite and almandine, more grossular and the same amounts of the pyrope and
majorite component as with the component sequence specified above.  Naturally, the sum of the ferric iron components must also be the same
with the two different allocation sequences: i.e. the sum of andridide + skiagite must be constant (the same) for the two alternative component
allocation sequences.

1. $Ca_{0.6}Fe^{2+}_{0.3}Mn_{0.1}Mg_{2.1}Al_{1.6}Fe^{3+}_{0.2}Si_{3.1}O_{12}$

Cation proportions ~ 80, norm. to 100%

Andr: $Ca_{0.3}Fe^{3+}_{0.2}Si_{0.3}$    3+2+3 = 8,   10%

Gros: $Ca_{0.3}Al_{0.2}Si_{0.3}$    3+2+3 = 8,   10%

Spes: $Mn_{0.1}Al_{0.067}Si_{0.1}$   1+0.67+1 = 2.67,  3.34%

Alm: $Fe^{2+}_{0.3}Al_{0.2}Si_{0.3}$    3+2+3 = 8    10%

Pyr: $Mg_{1.69}Al_{1.13}Si_{1.69}$     16.9+11.3+16.9 = 45.1,   56.4%

Maj (rest of Mg and Si): $Mg_{0.41}Si_{0.41}$  4.1+4.1 = 8.2,  10.3%

2. $Ca_{0.15}Fe^{2+}_{0.15}Mn_{0.15}Mg_{2.85}Al_{1.3}Fe^{3+}_{0.1}Si_{3.3}O_{12}$

Cation proportions ~ 80, norm. to 100%

Andr: $Ca_{0.15}Fe^{3+}_{0.1}Si_{0.15}$  1.5+1+1.5 = 4,   5%

~~Gros:~~ No more Ca

Spes: $Mn_{0.15}Al_{0.1}Si_{0.15}$    1.5+1+1.5 = 4,   5%

Alm: $Fe^{2+}_{0.15}Al_{0.1}Si_{0.15}$   1.5+1+1.5 = 4,   5%

Pyr: $Mg_{1.65}Al_{1.1}Si_{1.65}$     16.5+11+16.5 = 44,  55%

Maj (rest of Mg and Si): $Mg_{1.2}Si_{1.2}$ 12+12 = 24,   30%

3. $Ca_{0.3}Fe^{2+}_{0.6}Mg_{2.4}Al_{1.0}Fe^{3+}_{0.4}Si_{3.3}O_{12}$

Cation proportions ~ 80, norm. to 100%

Andr: $Ca_{0.3}Fe^{3+}_{0.2}Si_{0.3}$     3+2+3 = 8,   10%

~~Gross:~~ No more Ca

Skiag: $Fe^{3+}_{0.3}Fe^{3+}_{0.2}Si_{0.3}$    3+2+3 = 8,   10%

~~Spess:~~ No Mn

Alm: $Fe^{2+}_{0.3}Al_{0.2}Si_{0.3}$     3+2+3 = 8,   10%

Pyr: $Mg_{1.2}Al_{0.8}Si_{1.2}$     12+8+12 = 32,  40%

Majorite (rest of Mg and Si): $Mg_{1.2}Si_{1.2}$ 12+12 = 24,   30%

# 7. Melt residues, oceanic and orogenic peridotites and Archean cratonic lithosphere.

**a.** The simple FeO-MgO diagram in Fig. 7A shows the relations between melts and residues derived from melting of primitive mantle peridotites for various initial melting pressures and accumulated melt fractions. Fig 7B shows the composition and melt-extraction trends for various suites of oceanic and orogenic peridotites, plotted with MgO along the x-axis. Note that the melt extraction trends for FeO are quite flat for these pperidotites. Based on Fig 7A, give the expected

approximate initial melting pressure (or pressure range): **3 GPa** (or may be a range of 2.5-3.5 GPa)

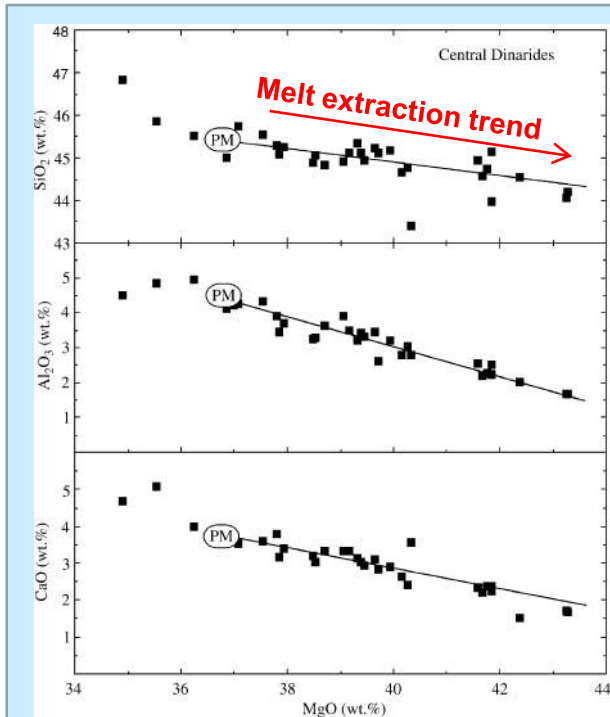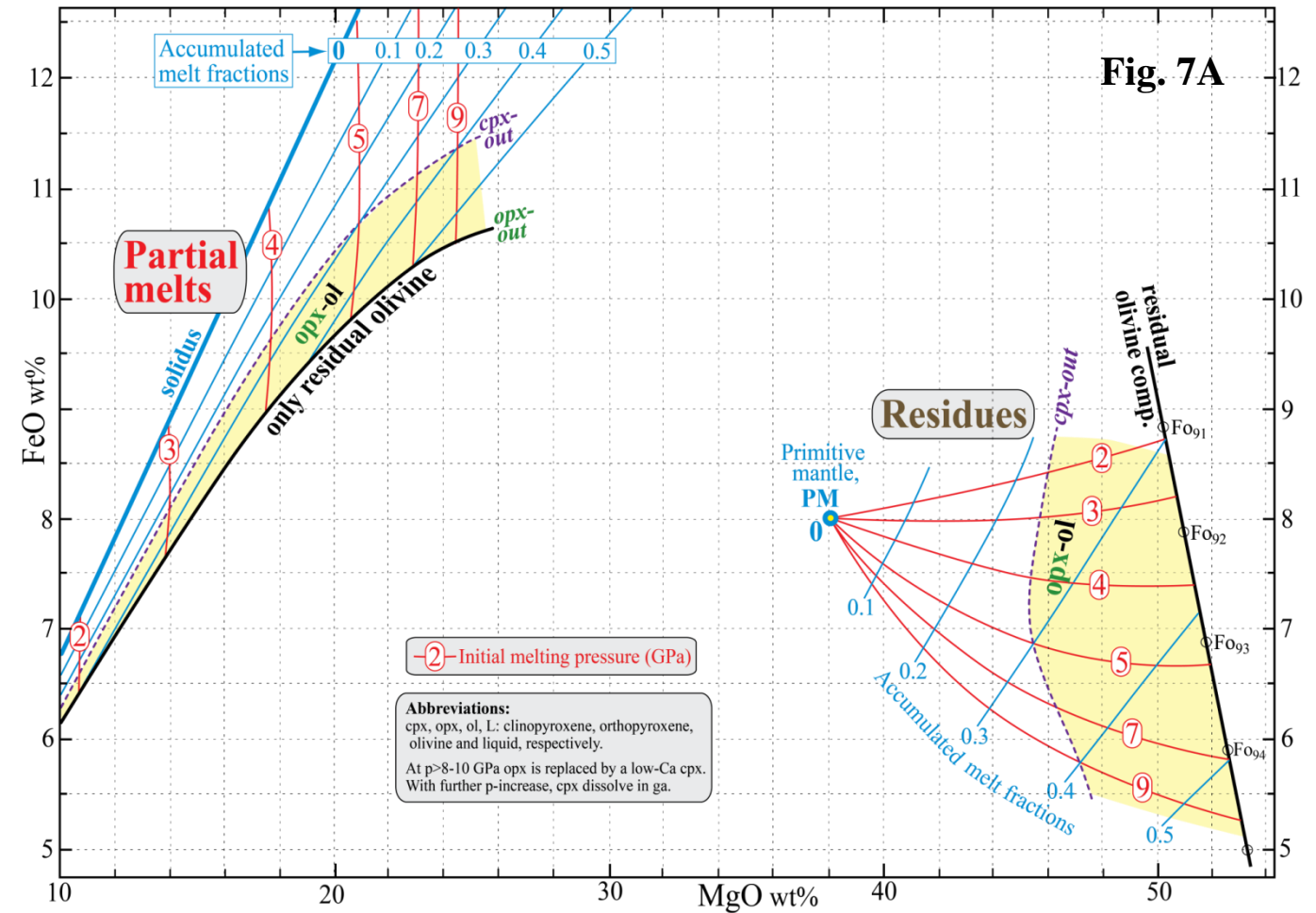and the approximate range of melt fractions (up to 45% MgO): **up to about 0.22** (i.e. 22%)



Fig. 7A

Fig. 7B