

Exercises

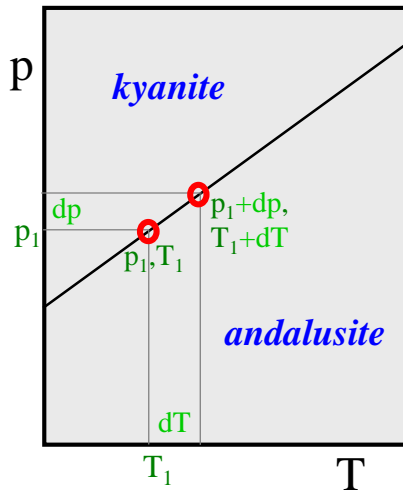
1. Clapeyron slope - general features. Although the indicated chemical reactions (below) are highly schematic, they must in principle be balanced. Subscripts _R and _P indicate reactants and products, respectively. A reaction written as e.g. $\text{Solids}_R = \text{Solids}_P$, might have one, or more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

a. Relate dT , dp , ΔS and ΔV 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.



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

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

2. Melting reaction: $\text{Solids}_R = \text{Melt}_P$

3. Devolatilisation reactions: $\text{Solids}_R = \text{Solids}_P + \text{fluid/vapour}$

e.g. $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2(\text{muscovite}) + \text{SiO}_2(\text{quartz}) = \text{KAlSi}_3\text{O}_8(\text{K-felspar}) + \text{Al}_3\text{SiO}_5(\text{kynaite}) + \text{H}_2\text{O}(\text{vapour})$

or: $\text{CaCO}_3(\text{calcite}) + \text{SiO}_2(\text{quartz}) = \text{CaSiO}_3(\text{wollastonite}) + \text{CO}_2(\text{vapour})$

2. Phase relations in the MgSiO_3 system. *The phases with compositions other than MgSiO_3 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?

b. Which of the two phases **LT-cpx** and **opx** is **most** compressible? _____.

c. Which of the two phases **mj** and **bm** has the the **largest** molar volume? _____.

d. Which of the phases **ak** and **bm** has the **largest** molar volume? _____.

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

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

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.

a: C: _____ **b:** C: _____ **a-b:** C: _____

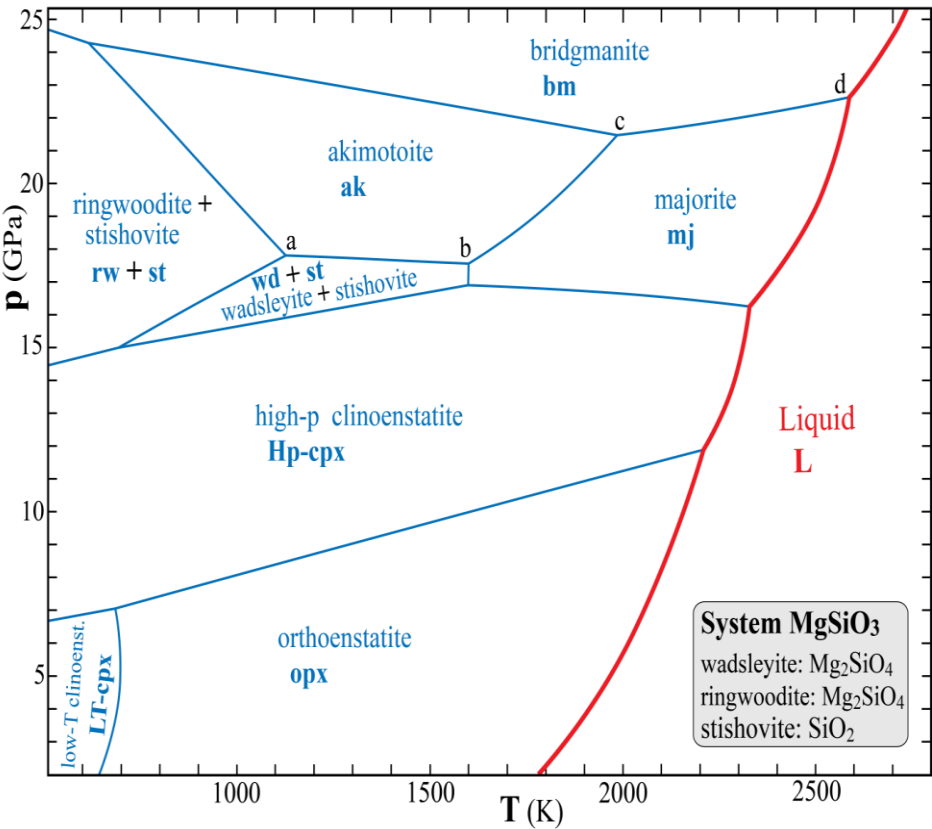
P: _____ P: _____ P: _____

F: _____ F: _____ F: _____

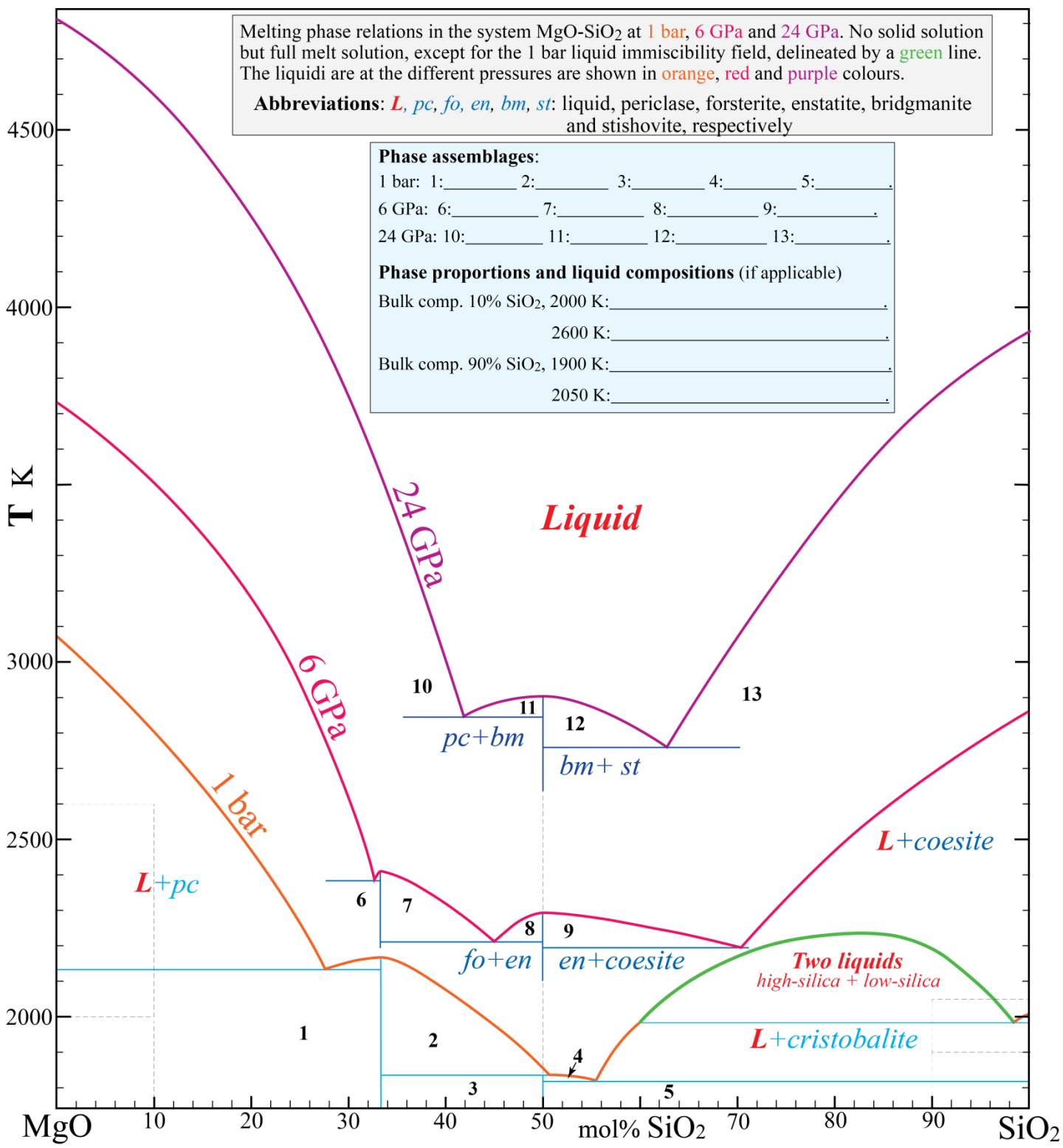
c: C: _____ **d:** C: _____ **c-d:** C: _____

P: _____ P: _____ P: _____

F: _____ F: _____ F: _____



- 3. Melting phase relations in the system MgO-SiO₂ - se further descriptions in the grey box.**
- Give the phase assemblages (without phase proportions and compositions, use the abbreviations) for the numbered field in the light blue box.
 - Give (blue box) the phase proportions and liquid compositions (if applicable) for bulk compositions with 10 and 90% SiO₂ at the indicated temperatures. You can give the liquid compositions as L_x, where X is mol% SiO₂.
 - Assume that a typical peridotite in this simple model system has 60% olivine and 40% orthopyroxene. Give the approximate model composition in mol% SiO₂ of such a peridotite:_____.
 - Mark the initial (invariant) melt compositions of such a model peridotite at 1 bar, 6 GPa and 24 GPa with small rings.
 - How does the invariant melt compositions of a peridotite in this system change with increasing pressure from 1 bar to 24 GPa? _____.



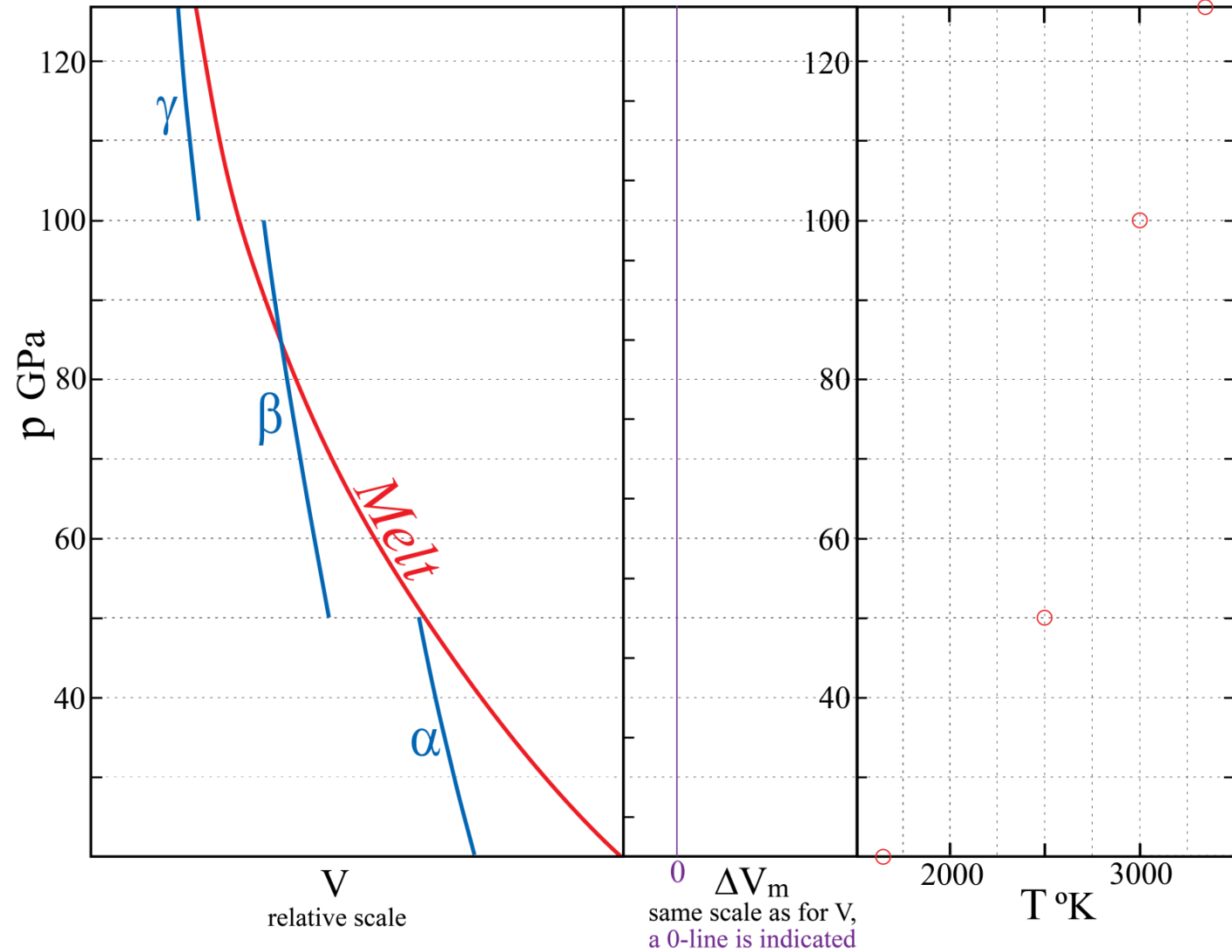
4. General features of melting curves, exemplified by an **imaginary one-component system** with three solid phases α , β and γ . The left figure panel shows the molar volume V for melt and solids (along the melting curve) as a function of pressure.

Melting reactions (solid \rightarrow 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 ΔS_m is **constant** in the problem below.

a. Draw ΔV_m as a function of pressure in the middle panel, using the same relative scale for the ΔV_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.**



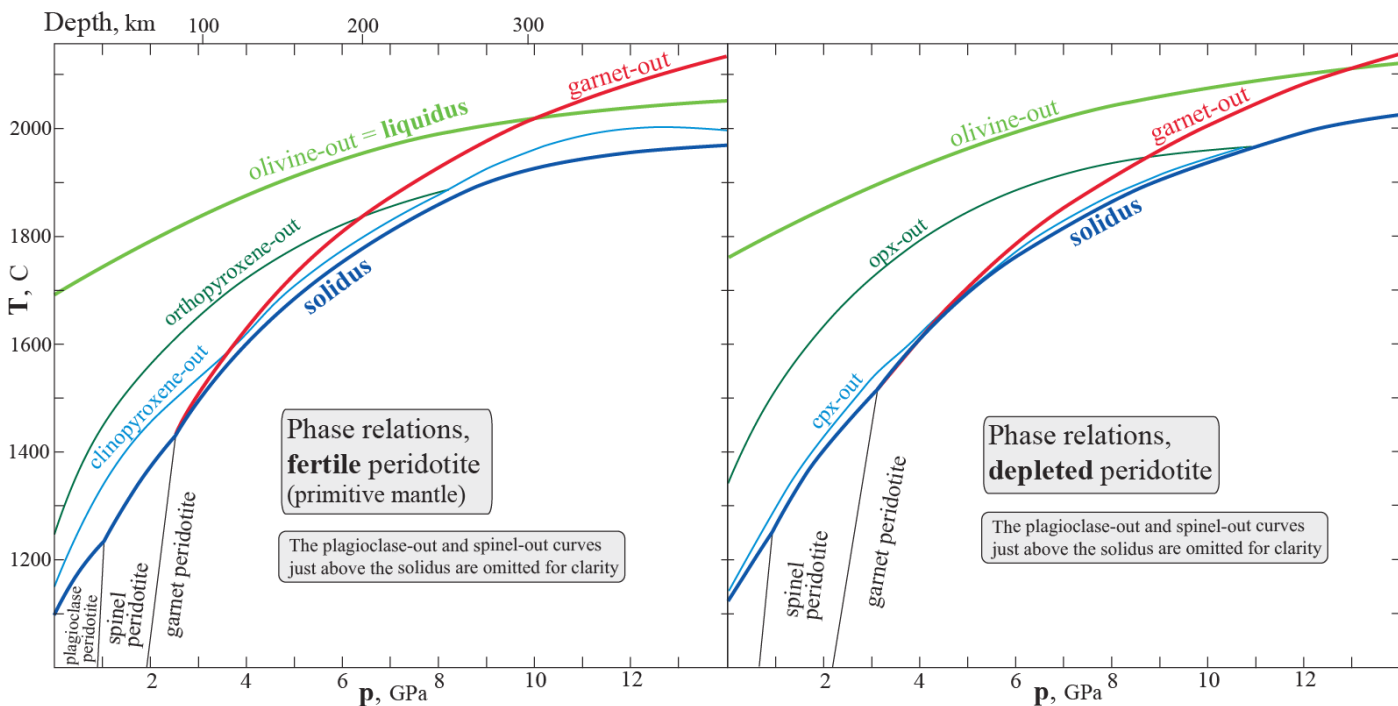
c. Explain briefly why pT-melting curves are almost always convex towards the liquid field?

d. ΔV_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: _____ and _____.

and the corresponding depth ranges (very approximate) where peridotitic melt would sink (be negatively buoyant):

_____ and _____.



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: $\text{CaO-MgO-AlO}_{1.5}\text{-SiO}_2$

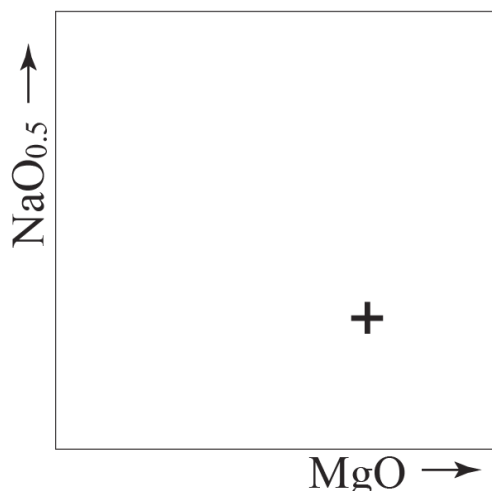
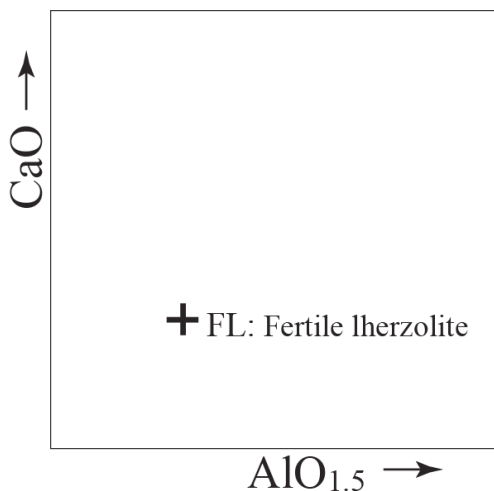
2) spinel to garnet lherzolite in the system: $\text{MgO-AlO}_{1.5}\text{-SiO}_2$

b. Based on the suprasolidus phase relations above, show the following **approximate** compositions (with correct relative positions) in the $\text{CaO-AlO}_{1.5}$ - and $\text{NaO}_{0.5}\text{-MgO}$ -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 $p < 6\text{-}8\text{ GPa}$?
(Note that melting will stop well before $p=0$)

The two main minerals: _____. Rock name: _____.



6. The system $\text{MgSiO}_3\text{-Al}_2\text{O}_3$ 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% Al_2O_3 , co_{80}), respectively.

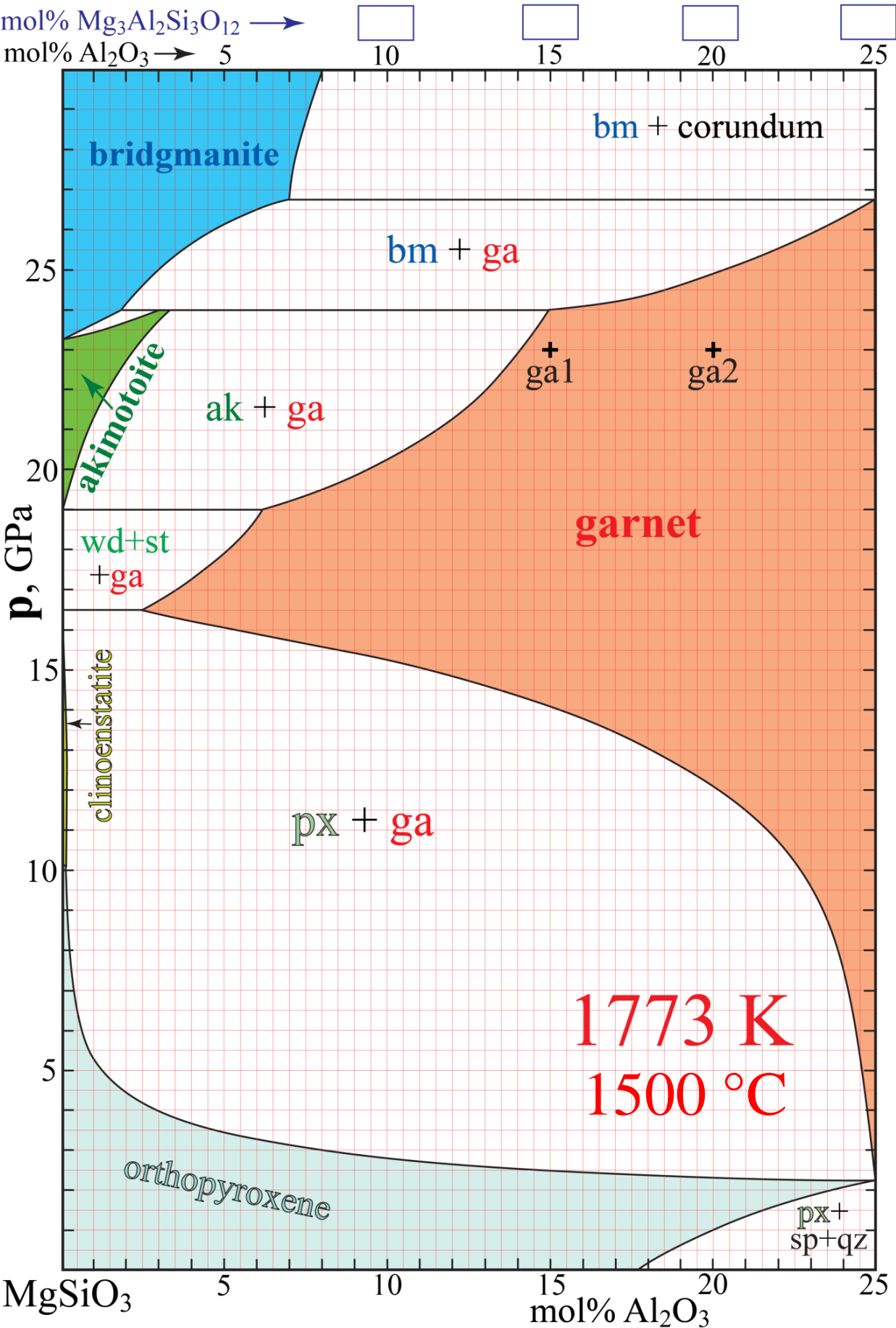


Fig. 6A

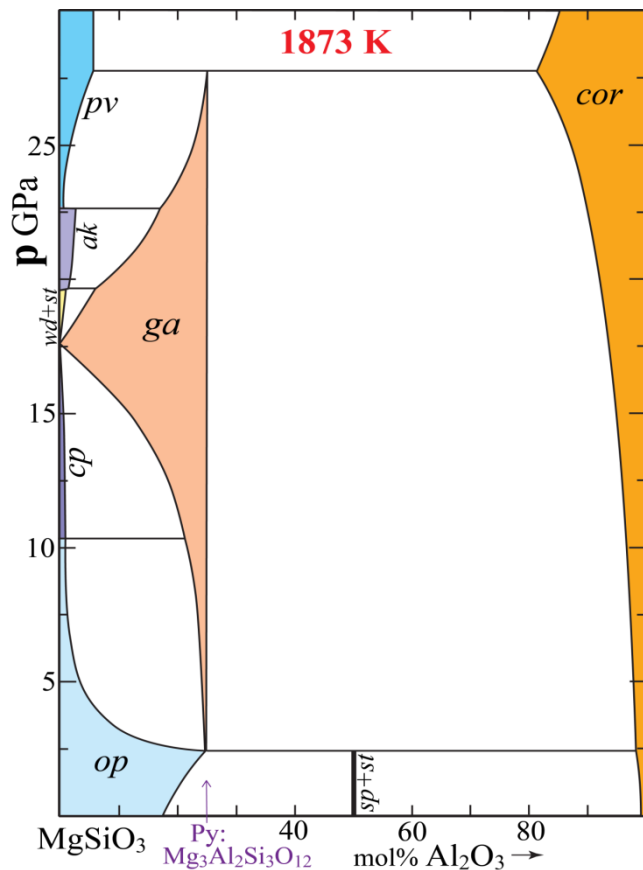


Fig. 6A

- 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: _____ coord.: _____ **B-site:** valence: _____ coord.: _____ **C-site:** valence: _____ coord.: _____.
- b. Explain briefly why garnet has 25 mol% Al_2O_3 as an **upper** limit, based on a simple crystallographic consideration.

- 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: _____ Si: _____ Mg: _____ **g2:** Al: _____ Si: _____ Mg: _____.

- 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: _____ 23.5 GPa: _____.

26.5 GPa: _____ 27.0 GPa: _____.

- f. At 1 GPa, the assemblage spinel+quartz ($MgAl_2O_4+SiO_2$) lies outside (to the right of) the shown phase diagram. Give mol% Al_2O_3 for this pure assemblage on the $MgSiO_3-Al_2O_3$ join: _____ and the mol ratio of sp/qz: _____.

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

_____ px + _____ (sp-qz) _____.

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 **bc₄₋₁₀** and **4-15 GPa**

C:

P:

F=

At **bc₀** and **16.5 GPa**

C:

P:

F=

In the range **bc₁₀₋₂₅** and **16-20 GPa**

C:

P:

F=

At **bc₀** and **19.0 GPa**

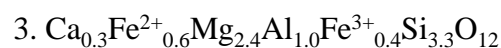
C:

P:

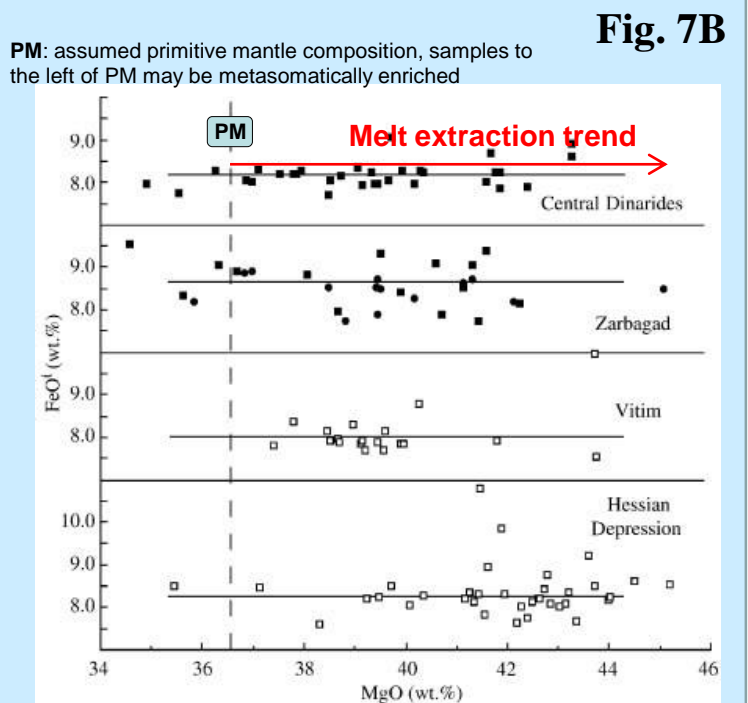
F=

h. What is the direct (and easy) indication of the presence of a majorite component (MgSiO_3 or $\text{Mg}_4\text{Si}_4\text{O}_{12}$) in a complex garnet formula ?

i. Calculate the proportions of the garnet end member components andradite, grossular, spessartine, almandine, pyrope and majorite ($\text{Mg}_4\text{Si}_4\text{O}_{12}$) 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, allocate the rest of the Fe^{3+} to the skiaegite component: $\text{Fe}^{2+}_3 \text{Fe}^{3+}_2 \text{Si}_3\text{O}_{12}$.



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):_____.

[illegible]

b. Figure 7C shows a xenolith-based geotherm from the Kaapvaal craton determined in the following way:

1. Geobarometry from the Al_2O_3 -content of orthopyroxene (opx) in equilibrium with garnet. The opx-solvus in Fig. 6 (problem 6) is fairly insensitive to temperature
2. Geothermometry from the opx-cpx-solvus (Fig. 7D, below, compositions on the enstatite wollastonite join)

You should determine the pressure of two garnet lherzolites with high $\text{Mg\#} = 100\text{Mg}/(\text{Mg}+\text{Fe})$ of 92-93 and the following key mineral compositions (we use the phase diagrams, Fig. 5 and Fig. 7D for the Fe-free systems in this problem):

Rock A: Opx with 3.0 mol% Al_2O_3 and cpx with 45.7 % Wo (wollastonite component)

Rock B: Opx with 0.6 mol% Al_2O_3 and cpx with 33.4 % Wo

Use the procedure above to estimate **first** the **pressure** of equilibration for rock A: _____, rock B: _____ and **then** the **temperature** of equilibration, using the correct cpx-solvus for rock A: _____, rock B: _____.

Using the following pressure-depth relation for the mantle: $\text{depth}(\text{km}) = p(\text{GPa})/0.03$, i.e. 200 km ~ 6 GPa, mark the approximate **positions of rocks A and B in Fig. 7C with small rings**. Which of the two rocks is most likely to have equilibrated in the asthenosphere: _____.

c. The gap in sampling of mantle xenoliths brought to the surface by kimberlites (see Fig. 7C) might be related to the occurrence of abundant carbonate minerals at the asthenosphere-lithosphere boundary region where kimberlite mmagmas are likely to form. Based on Fig. 7E, explain briefly why kimberlites are generally unable to bring carbonate-rich samples to the surface.

Geotherm based on mineral compositions in xenoliths from the Kaapvaal craton

