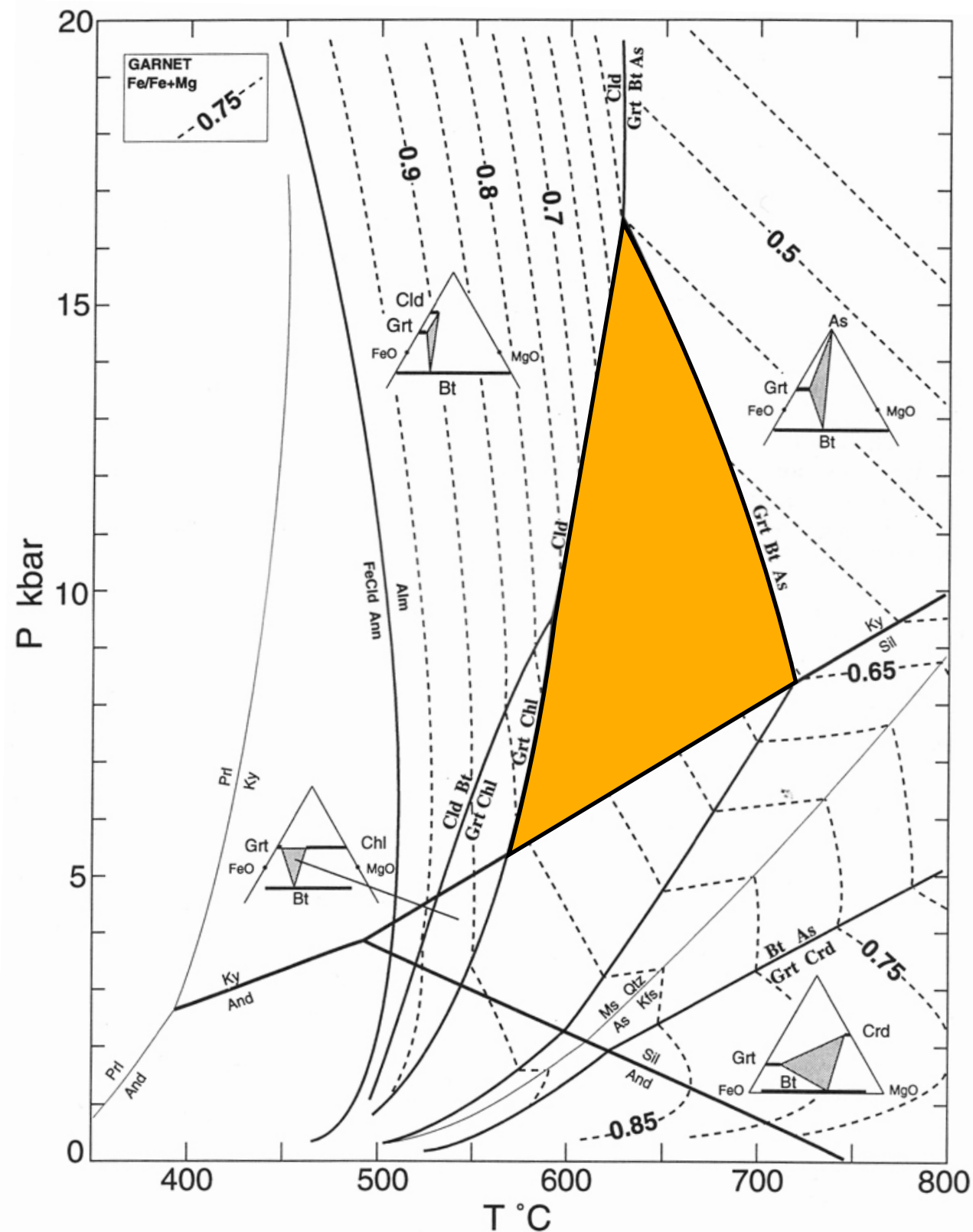


Lecture 13: GeoThermoBarometry



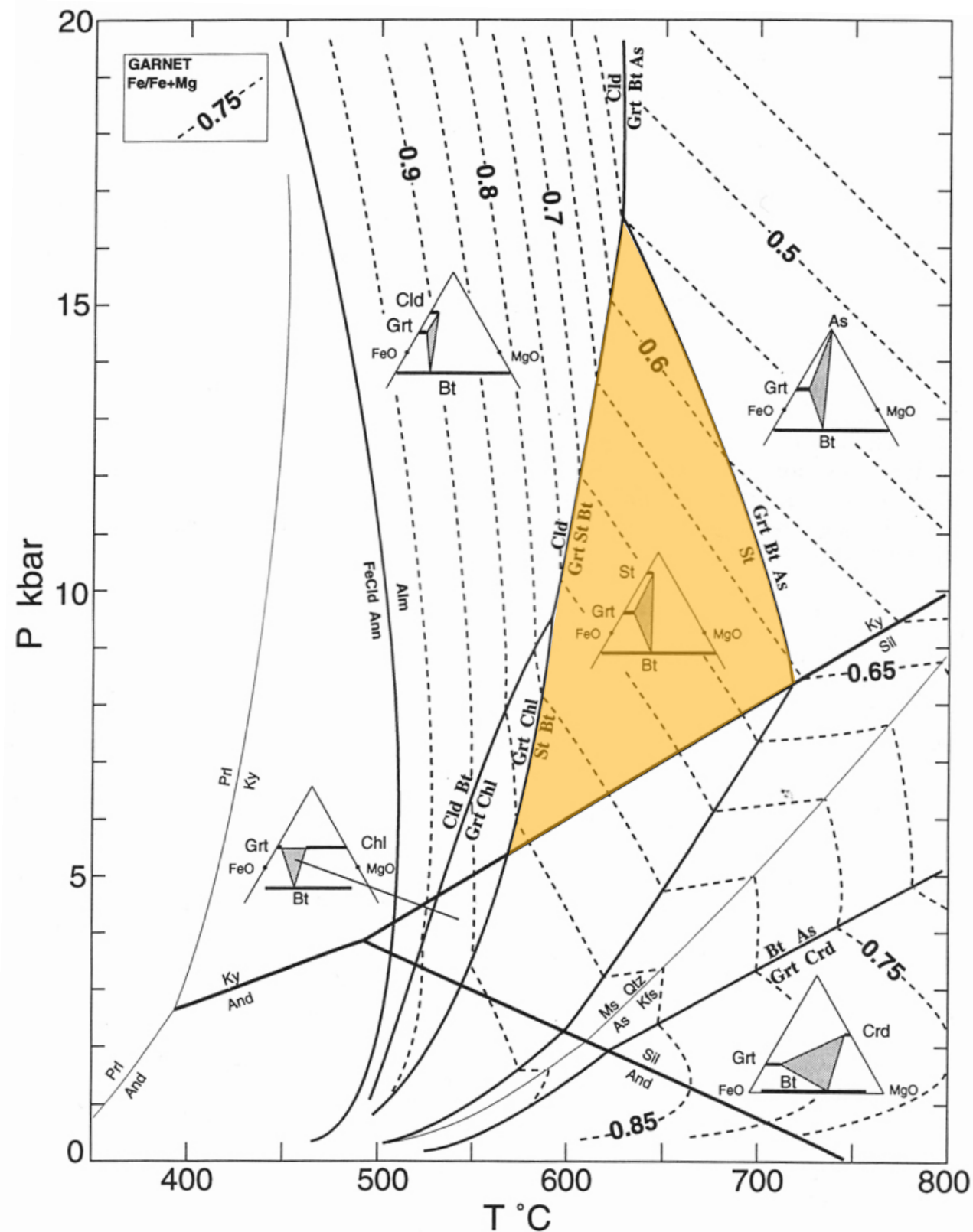
Petrogenetic grids divide up P - T space into fields with a stable paragenesis bounded by discontinuous reactions:

permits locating samples in P - T

However, most rocks are in a bivariate field: **only restrict P - T to a range, which can be large**

The yellow field has $Gt + St + Bt + Ms + Q$ at $T = 550 - 725$ °C and $P = 5 - 16$ kbar: all of the mid-crust

Mineral compositional contours



The composition of a solid solution mineral such as garnet will change in between the discontinuous reactions of a petrogenetic grid by continuous reactions:



This exchange is P-T dependent and so the equilibrium constant can be used to constrain T and/or P:

GeoThermoBarometry

GeoThermoBarometry

There are three several types of GeothermoBarometers:

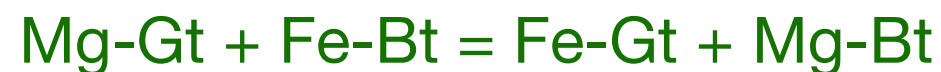
- Exchange reactions (e.g. $\text{Fe} \leftrightarrow \text{Mg}$ and $\text{Fe} \leftrightarrow \text{Mn}$ between Bt and Gt)
- Net transfer reactions (e.g. GASP: $\text{An} = \text{Gt} + \text{Al-sil} + \text{Qtz}$)
- Solubility thermobarometers (e.g. Zr in rutile; Ti in quartz)
- Solvus thermometry (e.g. the two-pyroxene and two-feldspar thermometers)
- Inter-sector thermometry (at present only calibrated for tourmaline)
- pseudosection-based thermobarometry: contours

Of these;

- exchange reactions are ideal as thermometers, because the ΔV_r is small (minimal dependence on pressure)
- net transfer reactions can have large ΔV_r and are therefore good barometers, but these generally require an estimate of T
- solubility and intersector thermometry only require one mineral and not a mineral paragenesis

Mg-Fe exchange thermometry

The exchange of Mg and Fe between coexisting ferromagnesian minerals turns out to be sensitive mostly to temperature, with only a minor pressure dependence



For this reaction; $\Delta G_r = \Delta H_r - T \cdot \Delta S_r + P \cdot \Delta V_r = -RT \ln K$ $K = \frac{X_{\text{Mg}}^3(\text{Bt}) \cdot X_{\text{Fe}}^3(\text{Gt})}{X_{\text{Fe}}^3(\text{Bt}) \cdot X_{\text{Mg}}^3(\text{Gt})}$

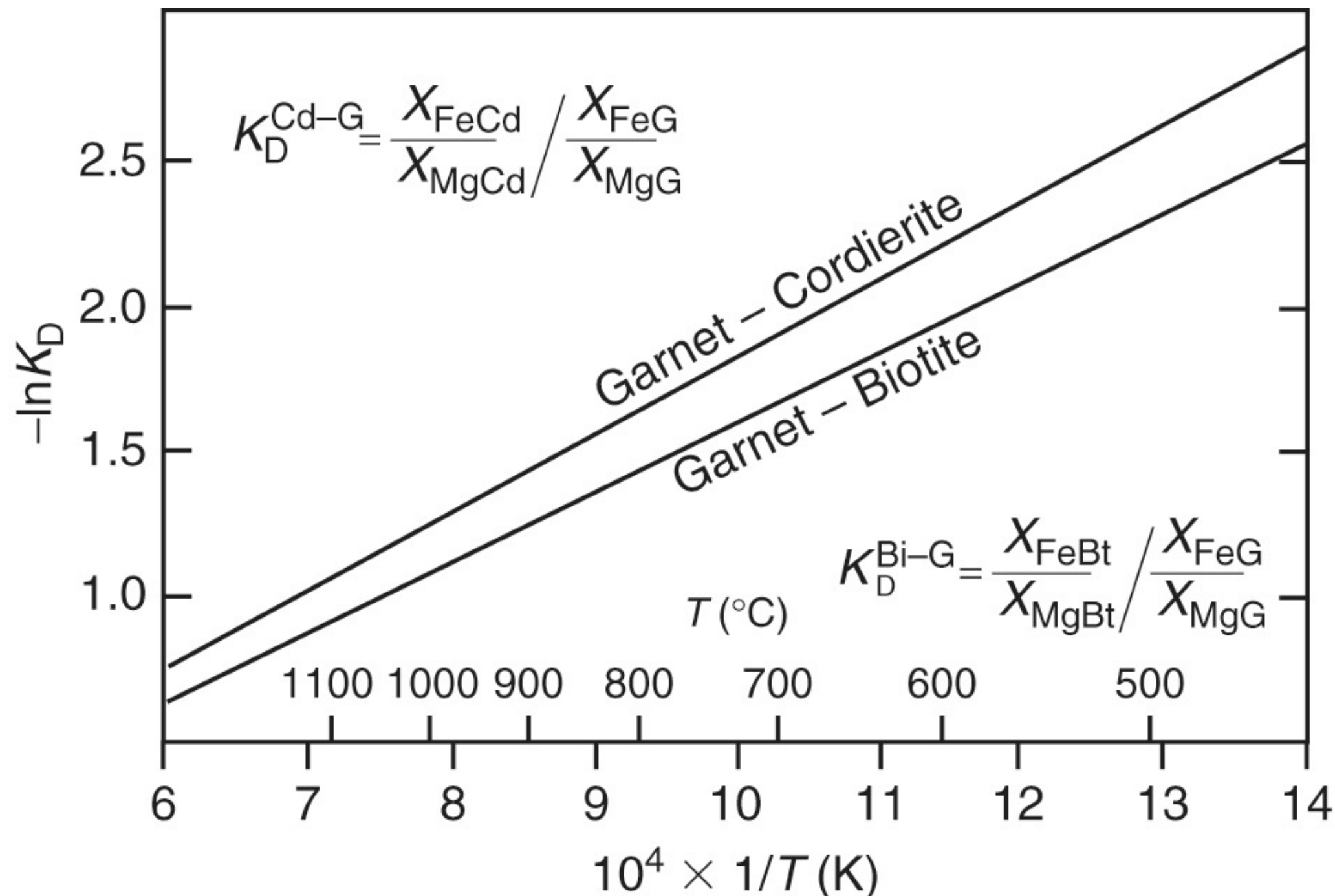
This can be re-arranged to: $\ln K = - \frac{\Delta H_r}{R} \frac{1}{T} + \frac{\Delta S_r}{R} - (P - 10^5) \cdot \frac{\Delta V_r}{RT}$

In this case ΔV_r is very small: $\ln K = - \frac{\Delta H_r}{R} \frac{1}{T} + \frac{\Delta S_r}{R}$, which is: $\ln K = a \frac{1}{T} + b$

Mg-Fe exchange thermometry

$$\ln K = - \frac{\Delta H_r}{R} \frac{1}{T} + \frac{\Delta S_r}{R}$$

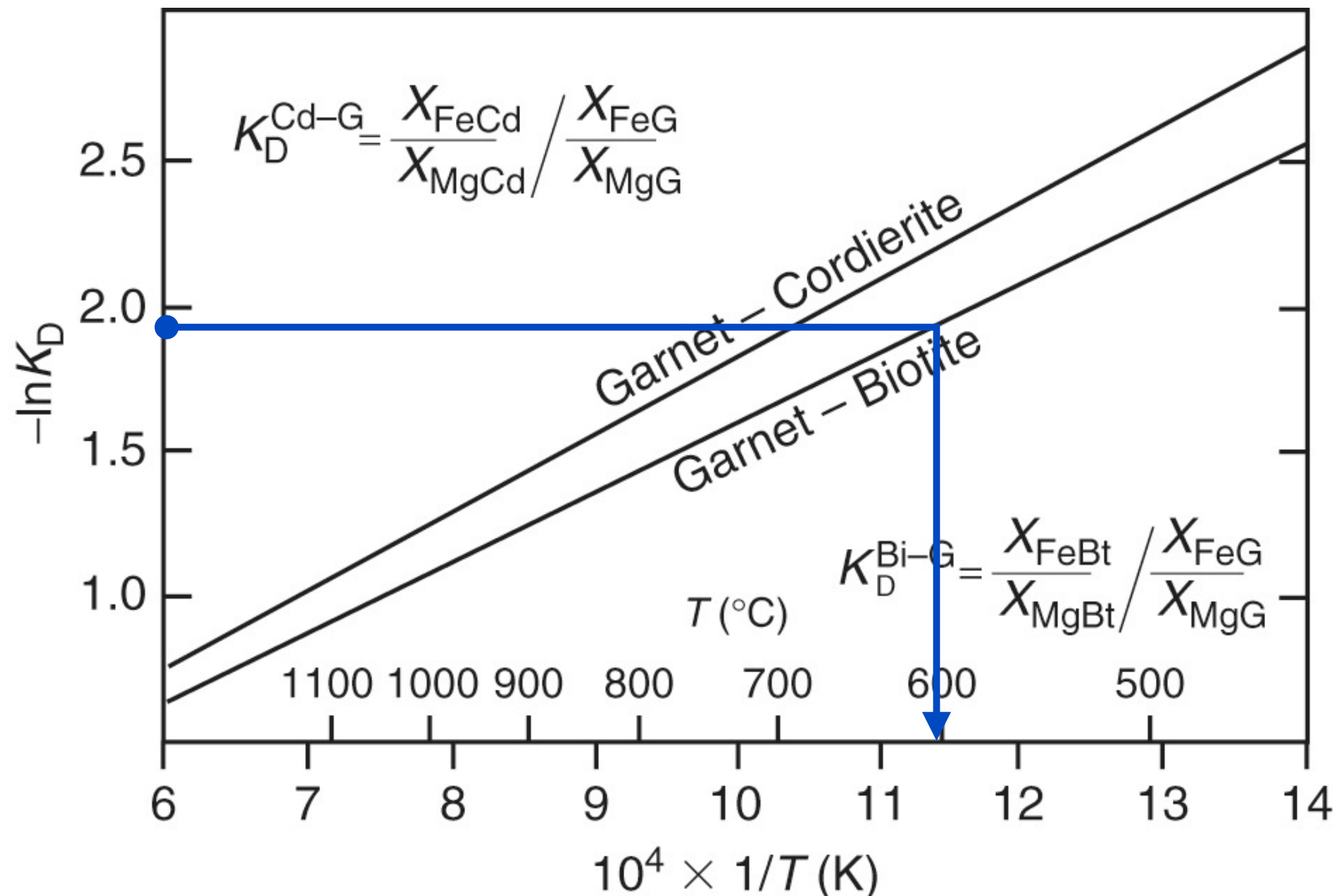
These $\ln K$ vs. T curves can be experimental, empirical or based on thermo data



Mg-Fe exchange thermometry

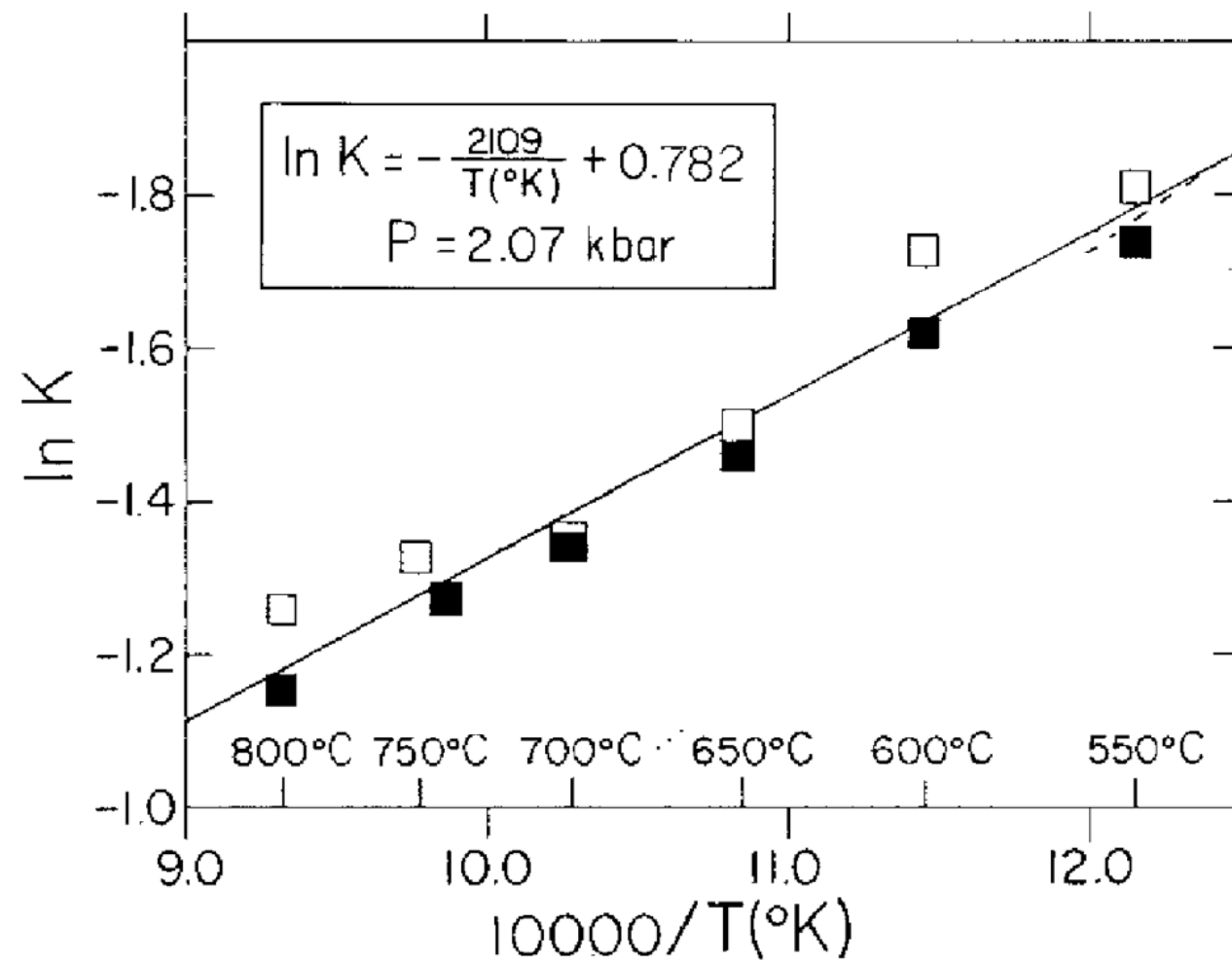
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These $\ln K$ vs. T curves can be experimental, empirical or based on thermo data

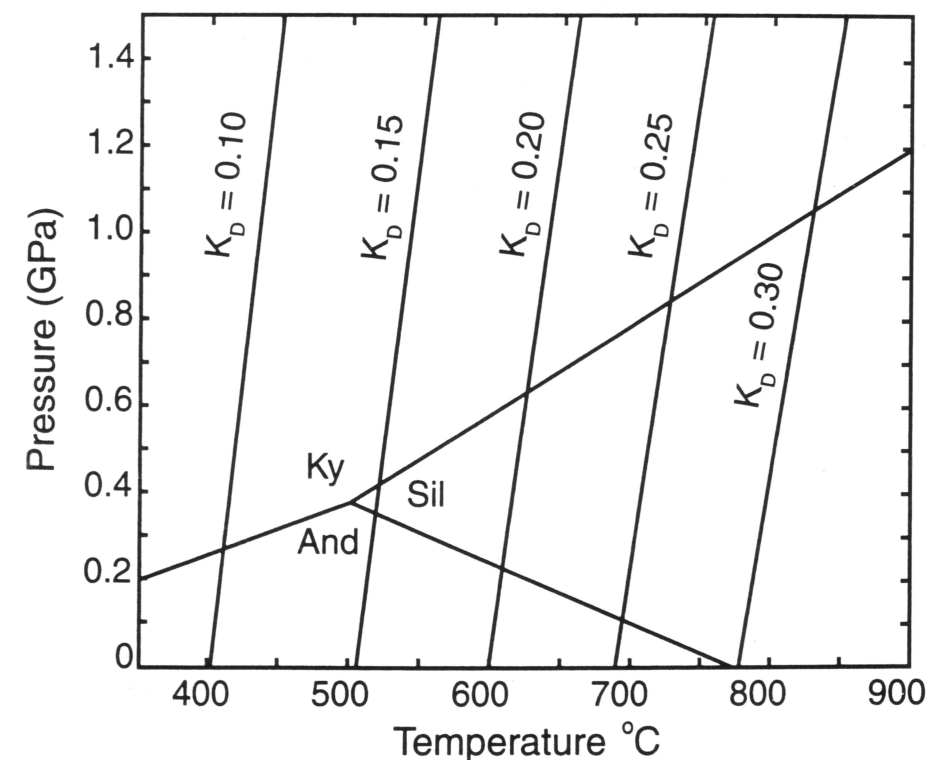


Mg-Fe exchange thermometry

Experimental data from Ferry and Spear (1978) for coexisting Bt and Gt



only limited P dependence:



Mg-Fe exchange thermometry

The thermometric formulation for garnet-biotite Mg-Fe exchange has been studied by many, and there are now several experimental and empirical formulations available:

Ferry and Spear (1978):

$$\ln K = -\frac{52108}{3R} \frac{1}{T} + \frac{19.51}{3R} - (P - 10^5) \cdot \frac{0.238 \cdot 10^{-5}}{3RT}$$

However

1. minor elements will modify the stability of Gt and Bt: Mn strongly stabilizes Gt and Ti stabilizes Bt: the $X_{Mn}(Gt)$ and $X_{Ti}(Bt)$ will therefore affect the temperatures
2. Gt and Bt are non-ideal thermodynamic solutions: $\Delta G (X_{Mg}=0.5) \neq 0.5 \Delta G_{Mg} + 0.5 \Delta G_{Fe}$

Dasgupta et al. (1991):

$$T(K) = 4301 + 3000 X_{Ca}Gt + 1300 X_{Mn}Gt - 495 (X_{Mg}Gt - X_{Fe}Gt) - 3595 X_{Al(VI)}Bt - 4423 X_{Ti}Bt + 1073 (X_{Mg}Bt - X_{Fe}Bt) + 0.02456 P / (1.85 - R \ln K)$$

The thermodynamics of solid solutions I

Most minerals are solid solutions; they are an intermediate composition within a set of end-member compositions:

Natural garnet: $\text{Ca}_{0.4}\text{Mg}_{0.8}\text{Fe}_{1.6}\text{Mn}_{0.2}\text{Al}_2\text{Si}_3\text{O}_{12}$

Garnet end-members:	grossular - $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	13 %
	pyrope - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	27 %
	almandine - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	53 %
	spessartine - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	7 %

If the garnet solid solution is an ideal mechanical mixture, we can calculate the thermodynamic properties of the natural garnet from proportional addition of the end-member properties:

enthalpy: $\Delta H_{\text{garnet}} = X_{\text{gr}} \cdot \Delta H_{\text{gr}} + X_{\text{py}} \cdot \Delta H_{\text{py}} + X_{\text{alm}} \cdot \Delta H_{\text{alm}} + X_{\text{spes}} \cdot \Delta H_{\text{spes}}$

volume: $\Delta V_{\text{garnet}} = X_{\text{gr}} \cdot \Delta V_{\text{gr}} + X_{\text{py}} \cdot \Delta V_{\text{py}} + X_{\text{alm}} \cdot \Delta V_{\text{alm}} + X_{\text{spes}} \cdot \Delta V_{\text{spes}}$

The thermodynamics of solid solutions II

Even when we are dealing with an ideal mechanical mixture, entropy cannot be calculated from a proportional combination of end-member entropies: **we add disorder**

entropy: $\Delta S_{\text{garnet}} = X_{\text{gr}} \cdot \Delta S_{\text{gr}} + X_{\text{py}} \cdot \Delta S_{\text{py}} + X_{\text{alm}} \cdot \Delta S_{\text{alm}} + X_{\text{spes}} \cdot \Delta S_{\text{spes}} + S_{\text{disorder}}$

For our natural garnet ($\text{Ca}_{0.13}\text{Mg}_{0.27}\text{Fe}_{0.53}\text{Mn}_{0.07}$)₃ $\text{Al}_2\text{Si}_3\text{O}_{12}$ only 13% of its 3 sites are occupied by Ca and there are many possible distributions of this Ca over the 3 sites

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Intuitively, this is what we expect to see:

S of mixture > S of pure mechanical mixture

S_{disorder} increases with degree of mixing

S_{disorder} depends on the number of sites over which an element can distribute

The thermodynamics of solid solutions III

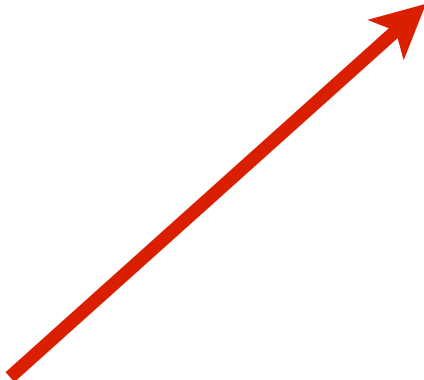
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$$S_{\text{mix}} = -n_{\text{sites}} R \sum_{i=1}^{n_{\text{comp}}} X_i \ln X_i$$

The thermodynamics of solid solutions III

entropy: $\Delta S_{\text{garnet}} = X_{\text{gr}} \cdot \Delta S_{\text{gr}} + X_{\text{py}} \cdot \Delta S_{\text{py}} + X_{\text{alm}} \cdot \Delta S_{\text{alm}} + X_{\text{spes}} \cdot \Delta S_{\text{spes}} + S_{\text{disorder}}$

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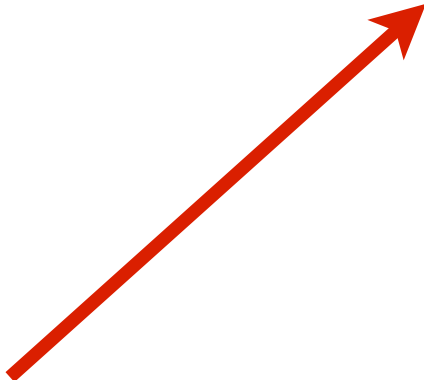


S of mixture > 0;
S increases due
to disorder

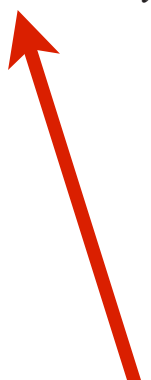
The thermodynamics of solid solutions III

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depends on the
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The thermodynamics of solid solutions III

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S increases due
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depends on the
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distribute

S_{mix} increases with
degree of mixing

$$X \ln X_{0.5,0.5} = -0.7$$
$$X \ln X_{0.9,0.1} = -0.3$$

Thermodynamics of an ideal solid solution

To calculate the ΔG of our natural garnet ($\text{Ca}_{0.4}\text{Mg}_{0.8}\text{Fe}_{1.6}\text{Mn}_{0.2}\text{Al}_2\text{Si}_3\text{O}_{12}$) :

$$\begin{aligned}\Delta G_{\text{garnet}} = & X_{\text{gr}} \cdot \Delta H_{\text{gr}} + X_{\text{py}} \cdot \Delta H_{\text{py}} + X_{\text{alm}} \cdot \Delta H_{\text{alm}} + X_{\text{spes}} \cdot \Delta H_{\text{spes}} \\ & - T \cdot [X_{\text{gr}} \cdot \Delta S_{\text{gr}} + X_{\text{py}} \cdot \Delta S_{\text{py}} + X_{\text{alm}} \cdot \Delta S_{\text{alm}} + X_{\text{spes}} \cdot \Delta S_{\text{spes}} \\ & \quad - 3R (X_{\text{gr}} \ln X_{\text{gr}} + X_{\text{py}} \ln X_{\text{py}} + X_{\text{alm}} \ln X_{\text{alm}} + X_{\text{spes}} \ln X_{\text{spes}})] \\ & + P \cdot (X_{\text{gr}} \cdot \Delta V_{\text{gr}} + X_{\text{py}} \cdot \Delta V_{\text{py}} + X_{\text{alm}} \cdot \Delta V_{\text{alm}} + X_{\text{spes}} \cdot \Delta V_{\text{spes}})\end{aligned}$$

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Unfortunately, many minerals of geological interest are not ideal solid solutions....

The mixing of the end-members cannot be described as simple mechanical mixing, but there is interaction among the elements (for example; the presence of Ca on one site, excludes the next from containing Mn)

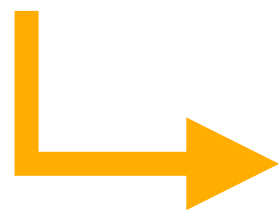
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Unfortunately, many minerals of geological interest are not ideal solid solutions....

The mixing of the end-members cannot be described as simple mechanical mixing, but there is interaction among the elements (for example; the presence of Ca on one site, excludes the next from containing Mn)



need to add a non-ideal contribution: ΔG_{excess}
 where $\Delta G_{\text{exc}} = \Delta H_{\text{exc}} - T \Delta S_{\text{exc}} + P \Delta V_{\text{exc}}$

Thermo of non-ideal mixtures: Margules parameters

In geology, we use so-called *Margules parameters* to quantify the non-ideal contribution to the Gibbs free energy of a solid solution:

For a simple two-component mixing the excess contributions would be

$$\Delta H^{\text{exc}} = X_1 X_2 \cdot W^{\text{H}}$$

$$S^{\text{exc}} = X_1 X_2 \cdot W^{\text{S}} \quad \text{where } W \text{ stands for the Margules parameter}$$

$$V^{\text{exc}} = X_1 X_2 \cdot W^{\text{V}}$$

$$\text{and so, } \Delta G^{\text{exc}} = \Delta H^{\text{exc}} - T S^{\text{exc}} + P V^{\text{exc}} = X_1 X_2 (W^{\text{H}} - T \cdot W^{\text{S}} + P \cdot W^{\text{V}})$$

Thermo of non-ideal mixtures: Margules parameters

If $\Delta G^{\text{exc}} = X_1 X_2 (W^{\text{H}} - T \cdot W^{\text{S}} + P \cdot W^{\text{V}})$, we make the assumption that the effect of mixing these components is equal in either direction

for example; mixing Mg into fayalite is equal to mixing Fe into forsterite

However, this is not likely as in the one case we're introducing a smaller cation and in the second a larger cation than the original cation on the site:

unlikely that the effect on the crystal structure is the same in both cases, so the W^{V} should be different

this can be accounted for by introducing non-equal W_{FaFo} and W_{FoFa}

now, $\Delta G^{\text{exc}} = X_1 X_2 (W_{12} X_2 + W_{21} X_1)$, with $W = W^{\text{H}} - T \cdot W^{\text{S}} + P \cdot W^{\text{V}}$

when $W_{12} = W_{21}$, this becomes $X_1 X_2 (X_2 + X_1) W_{21}$

and $X_1 + X_2 = 1$, so this becomes $X_1 X_2 W_{21}$, which is what we had before

An example: muscovite

What is the ΔG of muscovite of composition $K_{0.9}Na_{0.1}(Al_{1.8}Mg_{0.1}Fe_{0.1})Si_{3.2}Al_{0.8}O_{10}(OH)_2$

This muscovite is intermediate in composition among these 4 mica end-members

muscovite - $KAl_3Si_3O_8(OH)_2$
paragonite - $NaAl_3Si_3O_8(OH)_2$

Mg-phengite - $KMg_{0.5}Al_2Si_{3.5}O_8(OH)_2$
Fe-phengite - $KFe_{0.5}Al_2Si_{3.5}O_8(OH)_2$

part 1. The ideal Gibbs free energy:

$$\Delta G = X_{\text{musc}} \cdot \Delta G_{\text{musc}} + X_{\text{para}} \cdot \Delta G_{\text{para}} + X_{\text{Mgcel}} \cdot \Delta G_{\text{Mgph}} + X_{\text{Fecel}} \cdot \Delta G_{\text{Feph}}$$

$$\Delta H = X_{\text{musc}} \cdot \Delta H_{\text{musc}} + X_{\text{para}} \cdot \Delta H_{\text{para}} + X_{\text{Mgcel}} \cdot \Delta H_{\text{Mgcel}} + X_{\text{Fecel}} \cdot \Delta H_{\text{Fecel}}$$

$$V = X_{\text{musc}} \cdot V_{\text{musc}} + X_{\text{para}} \cdot V_{\text{para}} + X_{\text{Mgcel}} \cdot V_{\text{Mgcel}} + X_{\text{Fecel}} \cdot V_{\text{Fecel}}$$

$$S = X_{\text{musc}} \cdot S_{\text{musc}} + X_{\text{para}} \cdot S_{\text{para}} + X_{\text{Mgcel}} \cdot S_{\text{Mgcel}} + X_{\text{Fecel}} \cdot S_{\text{Fecel}} -$$

$$R (X_{\text{musc}} \cdot \ln X_{\text{musc}} + X_{\text{para}} \cdot \ln X_{\text{para}} + X_{\text{Mgcel}} \cdot \ln X_{\text{Mgcel}} + X_{\text{Fecel}} \cdot \ln X_{\text{Fecel}})$$

An example: muscovite

What is the ΔG of muscovite of composition $K_{0.9}Na_{0.1}(Al_{1.8}Mg_{0.1}Fe_{0.1})Si_{3.2}Al_{0.8}O_{10}(OH)_2$

$$\Delta G_{ideal} = X_{musc} \cdot \Delta G_{musc} + X_{para} \cdot \Delta G_{para} + X_{Mgcel} \cdot \Delta G_{Mgph} + X_{Fecel} \cdot \Delta G_{Feph}$$

part 2. The non-ideal contribution to Gibbs free energy

Green & Usdansky (1986) give Margules parameters for the muscovite solid solution, but only for Musc and Para so will assume that others are 0

$$RT \ln \gamma_{musc} = (1 - X_{musc})^2 (W_{musc} + 2X_{musc} (W_{para} + W_{musc}))$$

$$RT \ln \gamma_{para} = (1 - X_{para})^2 (W_{para} + 2X_{para} (W_{musc} + W_{para}))$$

this is the same as $\Delta G_{exc} = X_{musc}X_{para} (W_{para}^G X_{musc} + W_{musc}^G X_{para})$

$$W_{musc}^G = 19456 + 1.6543 T - 0.4561 P$$

$$W_{para}^G = 12230 + 0.7104 T + 0.6653 P$$

$$\begin{aligned} \Delta G_{muscovite} = \Delta G_{ideal} + \Delta G_{exc} = & X_{musc} \cdot \Delta G_{musc} + X_{para} \cdot \Delta G_{para} + X_{Mgcel} \cdot \Delta G_{Mgph} + X_{Fecel} \cdot \Delta G_{Feph} \\ & + X_{musc}X_{para} (W_{para}^G X_{musc} + W_{musc}^G X_{para}) \end{aligned}$$