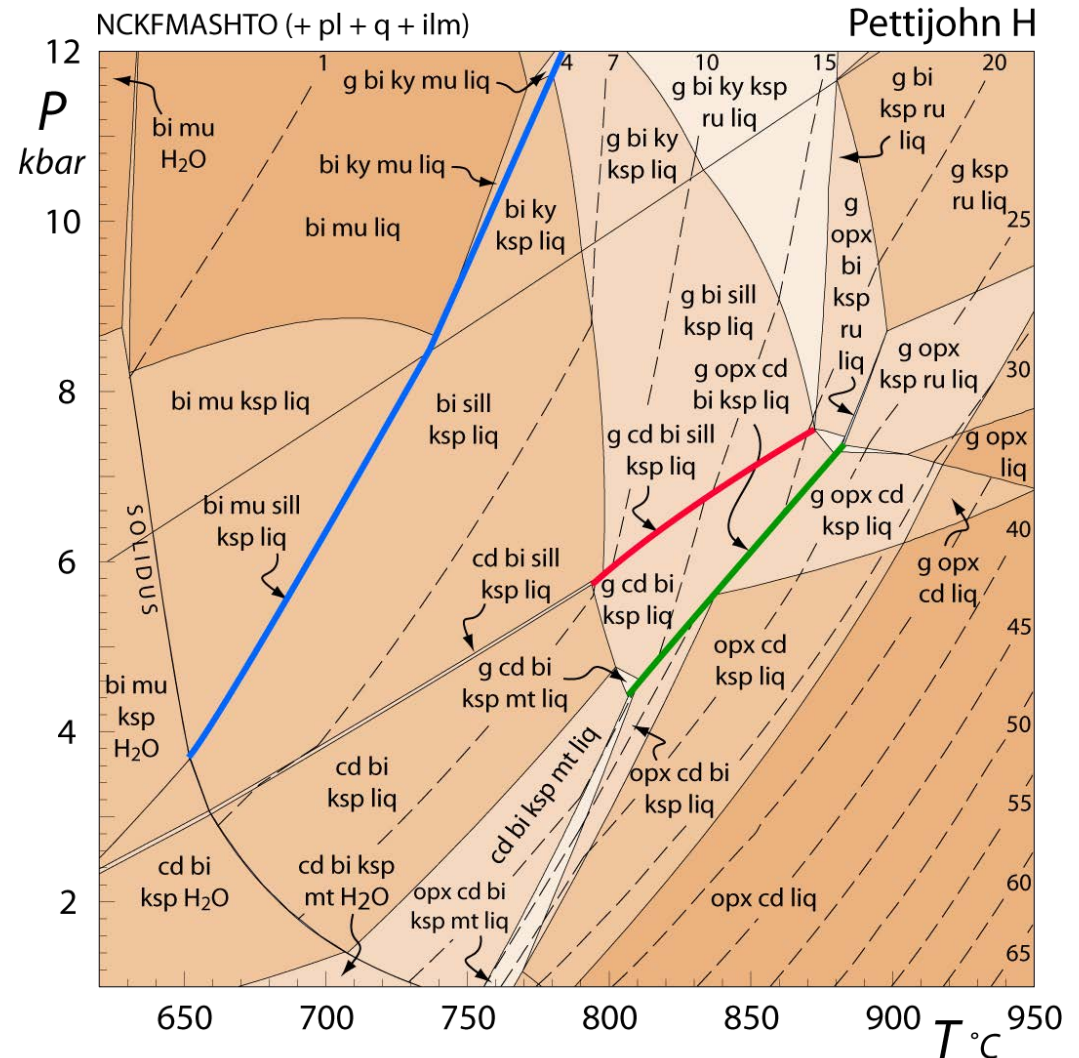


Tim JOHNSON



Curtin University

THE INSTITUTE FOR
GEOSCIENCE RESEARCH (TIGeR)



COMMONWEALTH OF AUSTRALIA

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The plan

DAY 1

- An intro to thermodynamics
- An intro to THERMOCALC
- Exercise 1 intro

DAY 2

- Tips and tricks
- Exercise 1 finish (?)
- Whatever



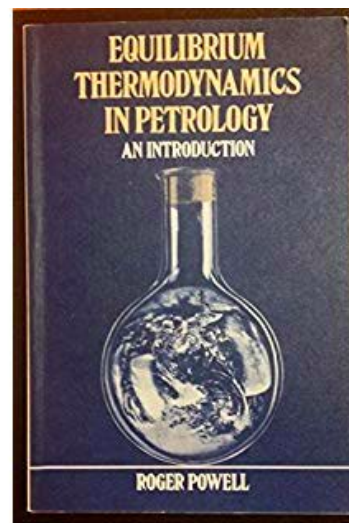
Prologue:

What are we doing here?

What information is in (metamorphic) rocks?

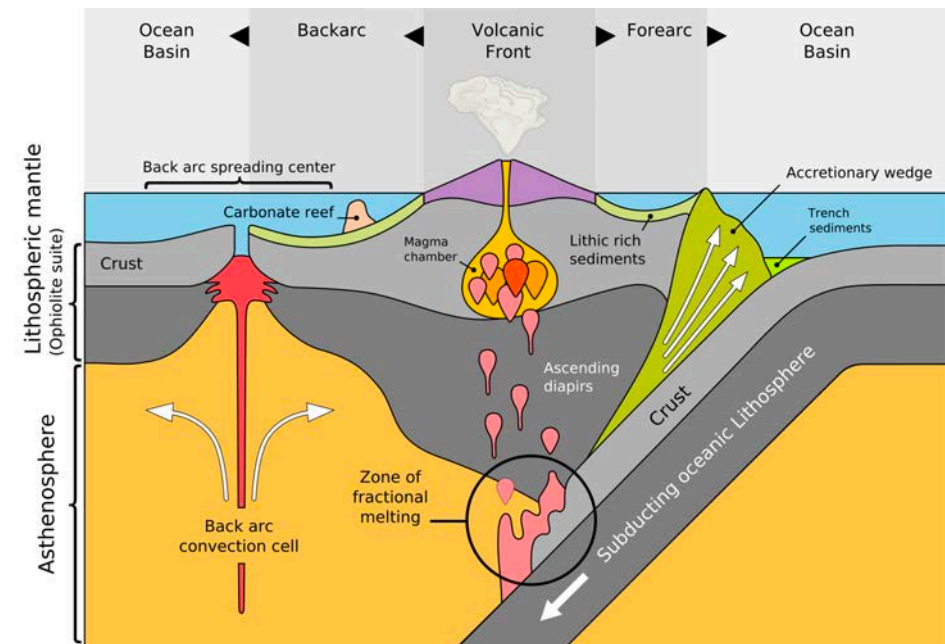
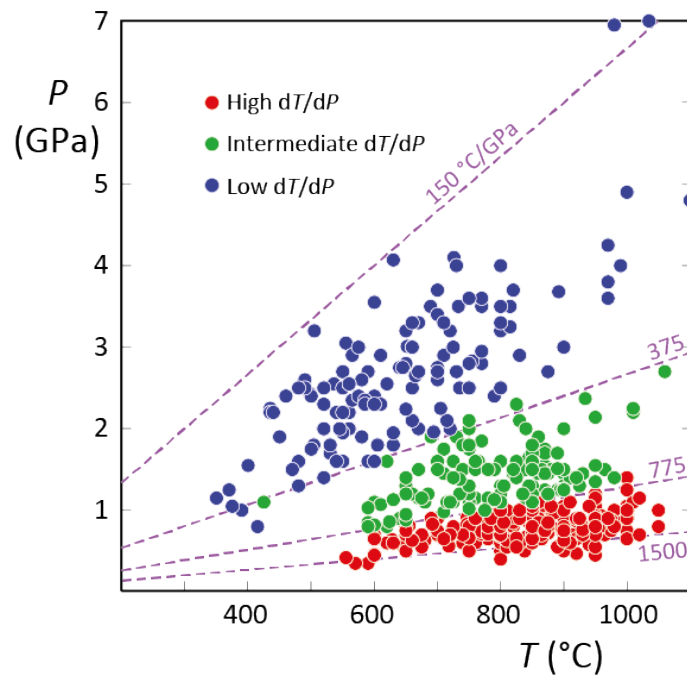
Preface to Powell (1978) 'Equilibrium Thermodynamics in Petrology: An Introduction':

The basic premise in this book is that at least some of the features in many rocks can be interpreted as the result of the achievement of equilibrium on some scale at some time or times during their evolution. Given this premise, equilibrium thermodynamics provides a way of looking at rocks, not only for discovering at what conditions they formed, for example the temperature and pressure of formation, but also for understanding the processes involved in their formation.



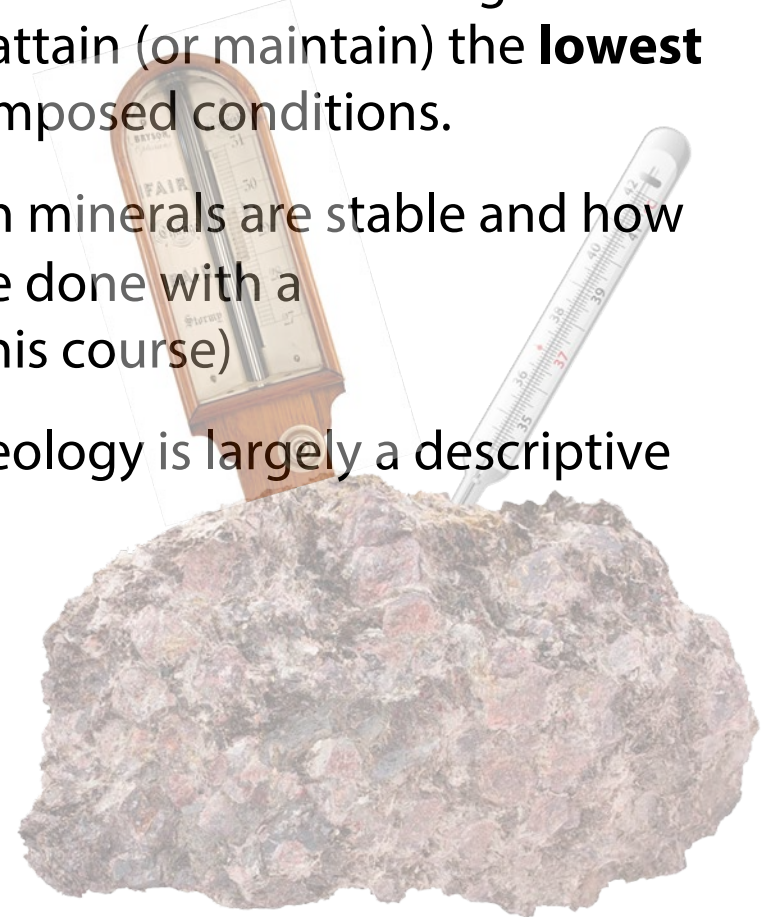
Why bother with metamorphic rocks?

- Different tectonic settings are characterised by different heat flow (thermal) regimes,
- The metamorphic rocks/assemblages developed in different tectonic settings can be characteristic.



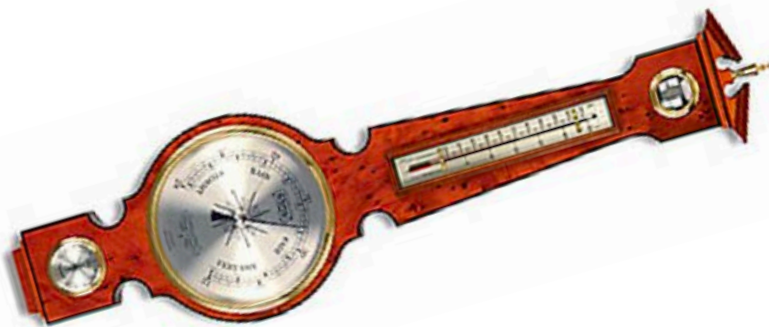
Why bother with metamorphic rocks?

- Metamorphic petrology is the study of mineralogical and textural changes that occur within a rock in response to superimposed conditions such as **pressure** and **temperature** within the Earth's crust.
- Metamorphism—changes to minerals and/or mineral assemblages—is driven by the chemical system wanting to attain (or maintain) the **lowest energy configuration** for the (changing) imposed conditions.
- Expressing, in a quantitative manner, which minerals are stable and how their chemical compositions change can be done with a **thermodynamic approach** (the point of this course)
- Without thermodynamics, metamorphic geology is largely a descriptive science



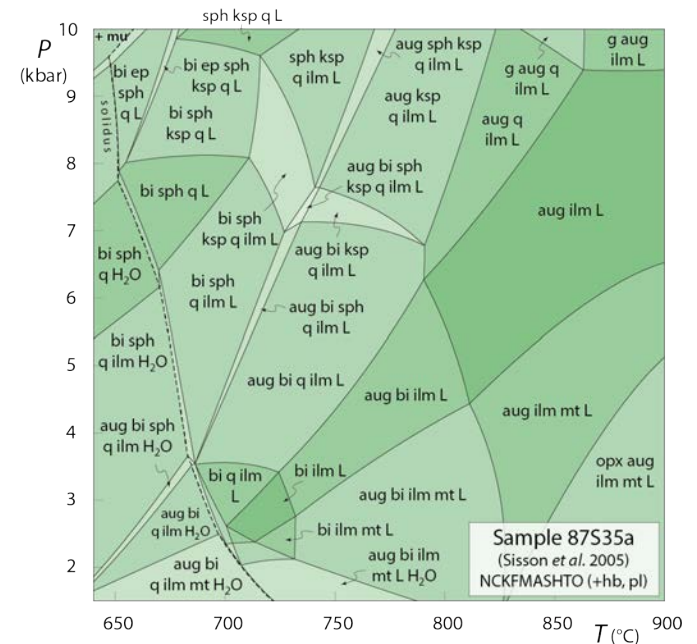
Thermobarometry

- Quantitative metamorphic petrology is largely concerned with constraining the pressure (P) and temperature (T) at which a rock attained equilibrium = **thermobarometry**
- Conventional thermobarometry** uses the constituent minerals in a rock to back-calculate the conditions of their formation = **INVERSE MODELLING**.
- Alternatively, the bulk composition of a rock can be used to predict which minerals should be present under particular conditions = **FORWARD MODELLING**

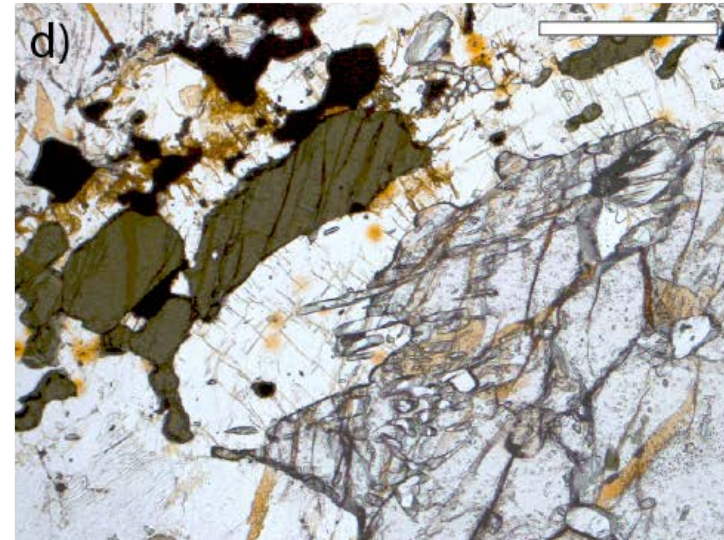
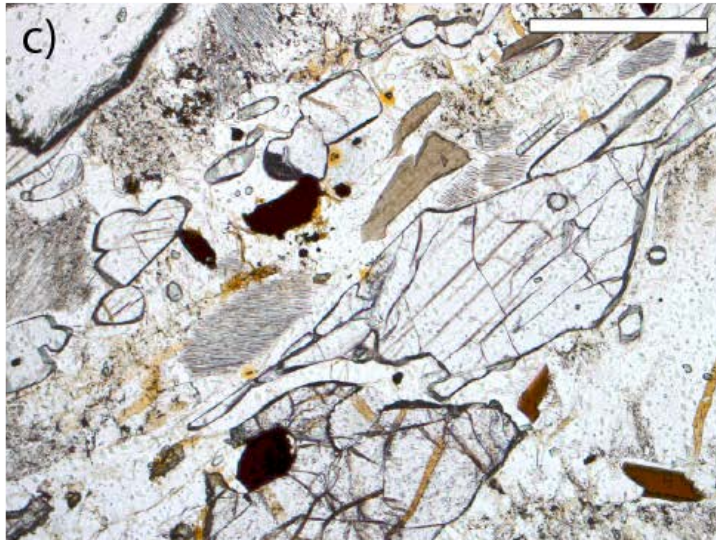
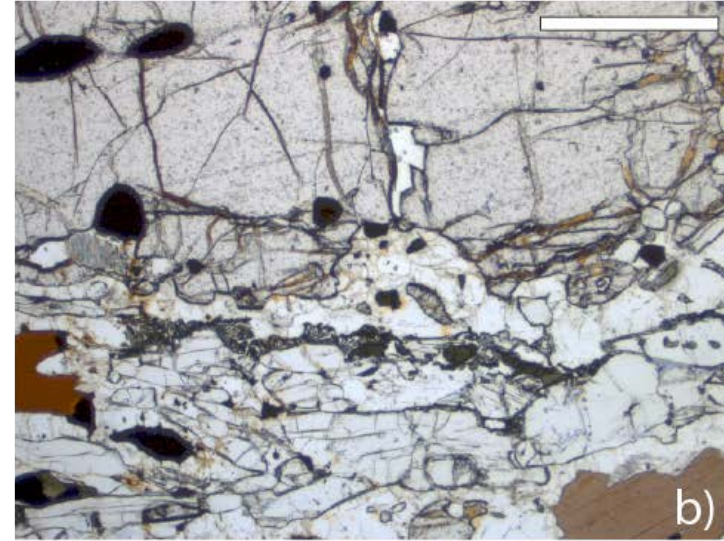


What is PEM and why bother?

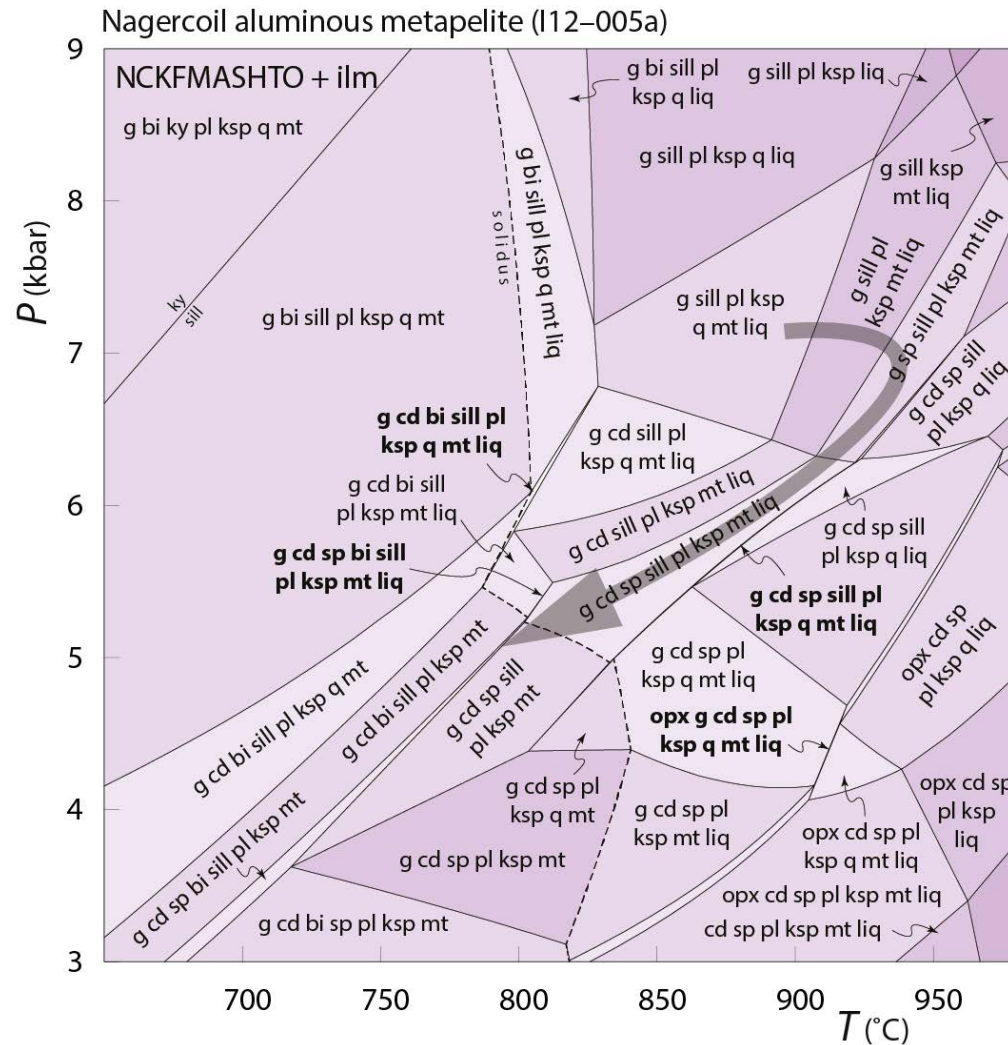
- **Phase equilibrium modelling** (PEM) uses the **measured composition of a system** (a rock) to predict which phases will be stable as a function of (mostly) pressure (P) and temperature (T) = **FORWARD MODELLING**
- PEM permits the quantitative investigation of **processes**, including:
 - path-specific metamorphism (i.e., specified geotherms)
 - the role of fluids (e.g., internal vs external buffering);
 - metasomatism;
 - melting and melt loss;
 - fractional crystallisation;
 - microstructure development;
 - etc..



Making sense of petrographic observations....



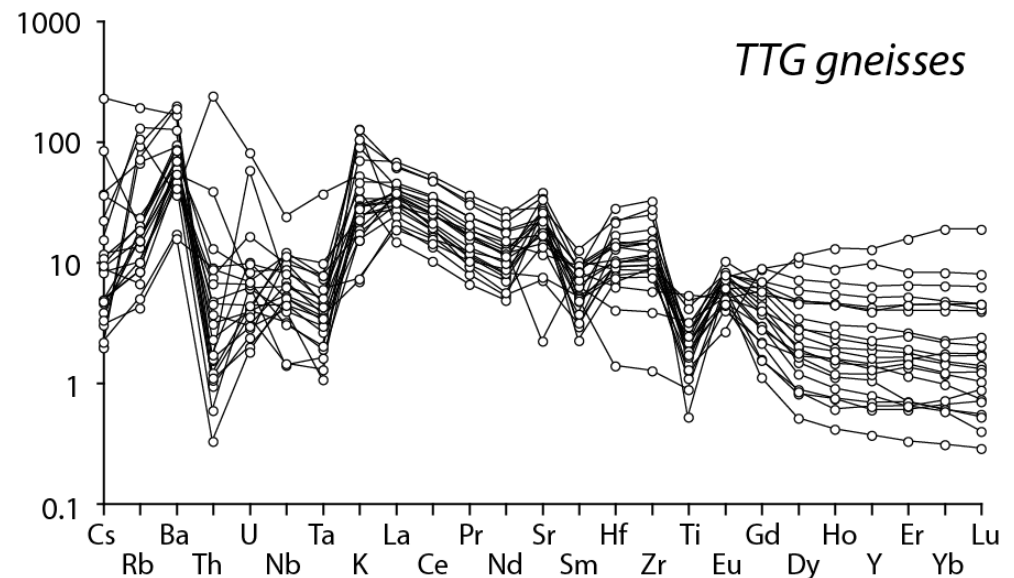
To constrain P–T evolution



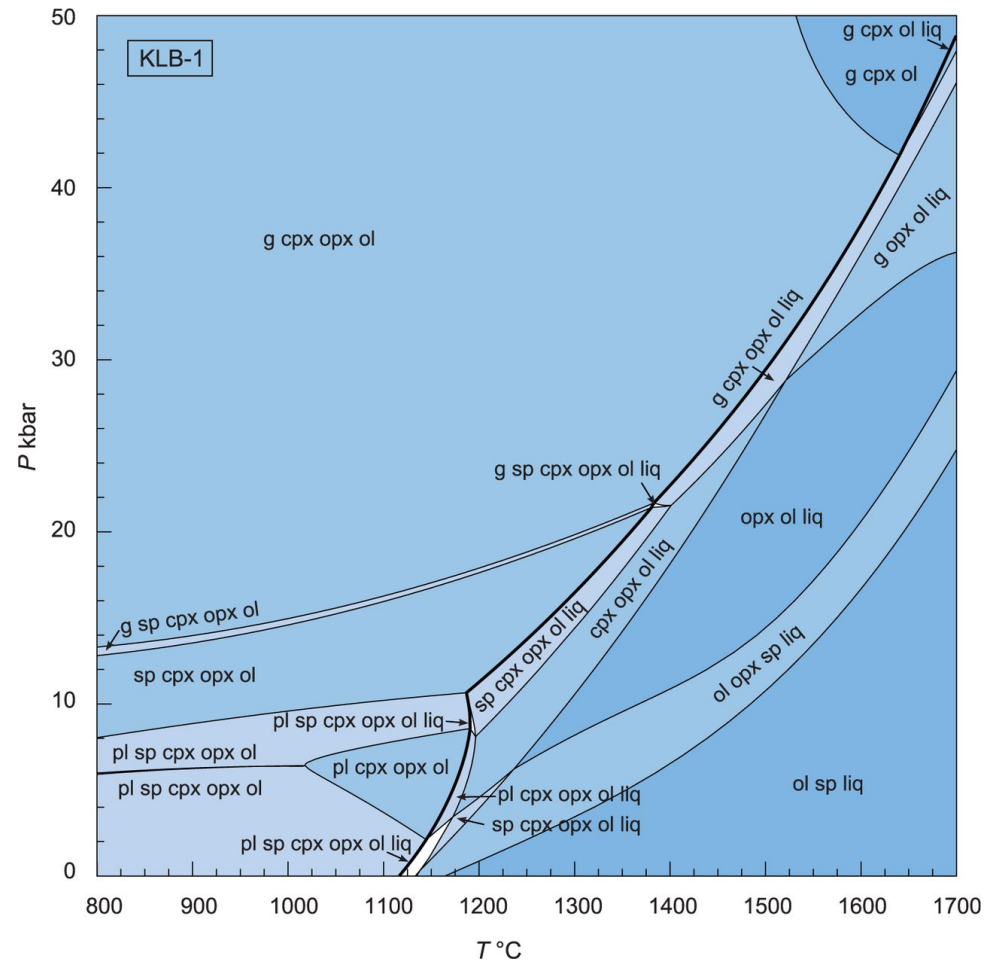
- Inferred peak minerals constrain peak P - T conditions
- Retrograde minerals help constrain post-peak evolution
- Inclusions can help constrain prograde evolution
- Lots more is possible...

What is PEM and why bother?

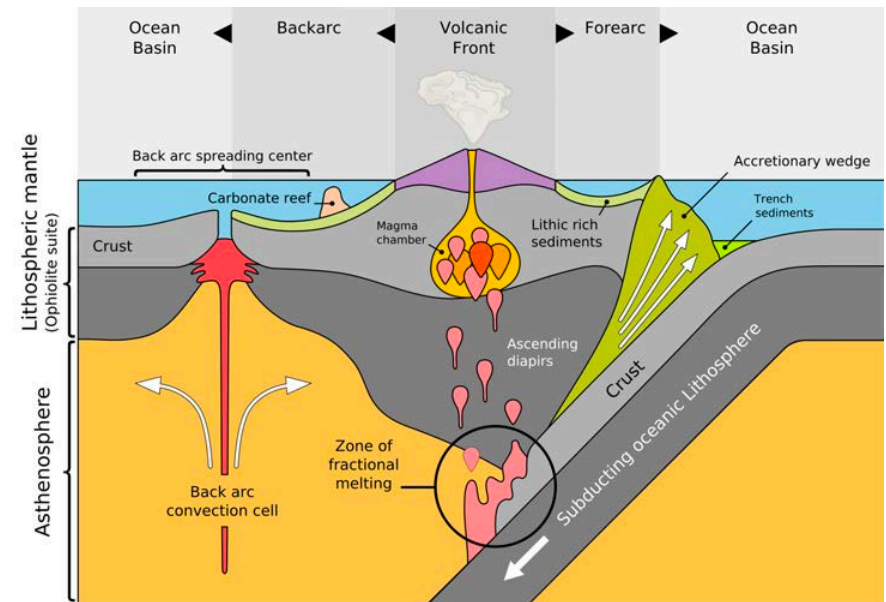
- Although it predicts which minerals are stable using (mainly) **major element** data, we understand increasingly well the mineralogical effects on **trace element** partitioning
- The derived conditions, in particular P and T and $\delta P/\delta T$, when combined with age (isotopic) and other geochemical data, can tell us about **process**



Not just metamorphism...

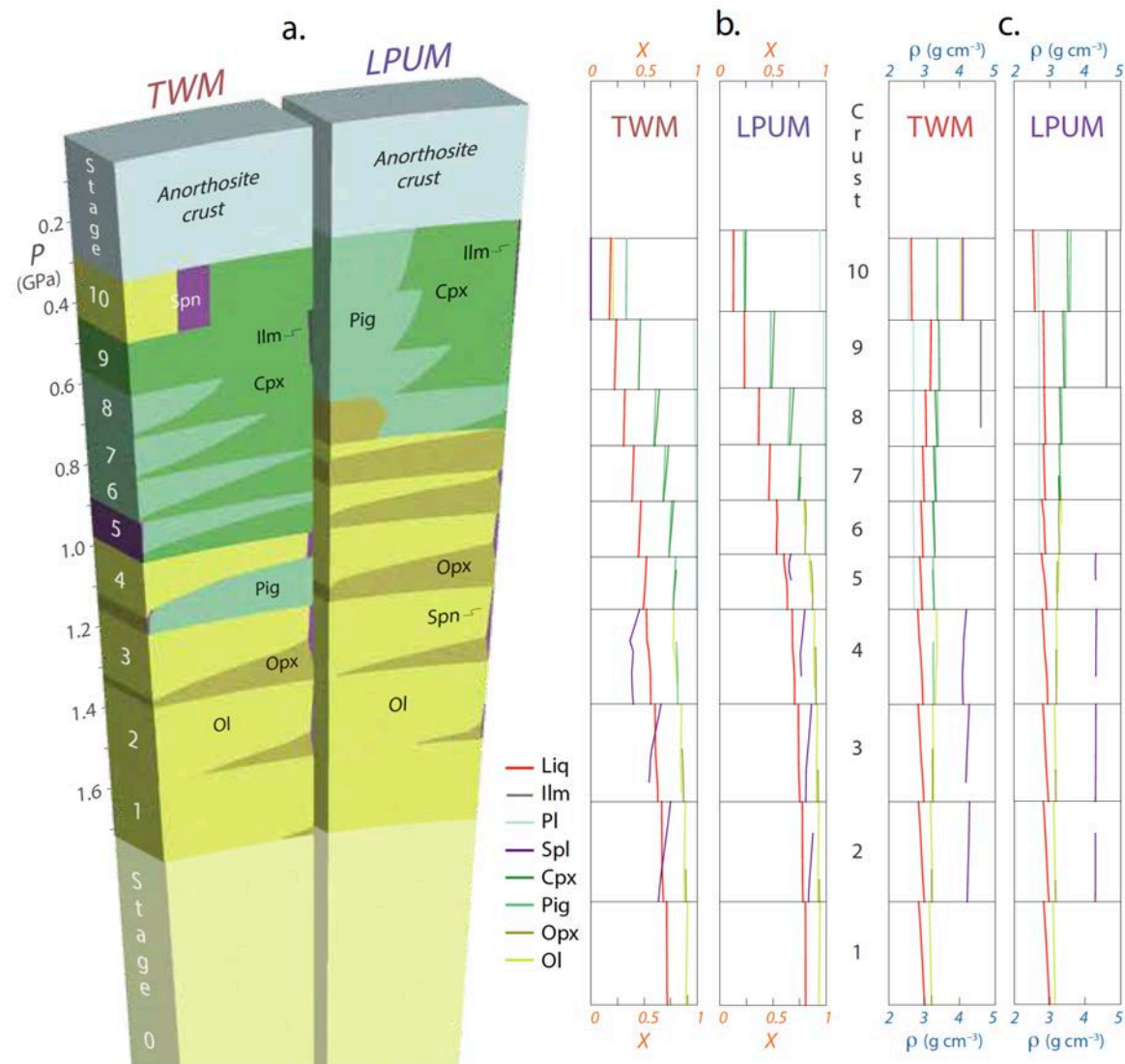


From Jennings & Holland (2015)



Tim Johnson, THERMOCALC short course, 2021

Or Earth processes...



From Johnson et al. (2021)

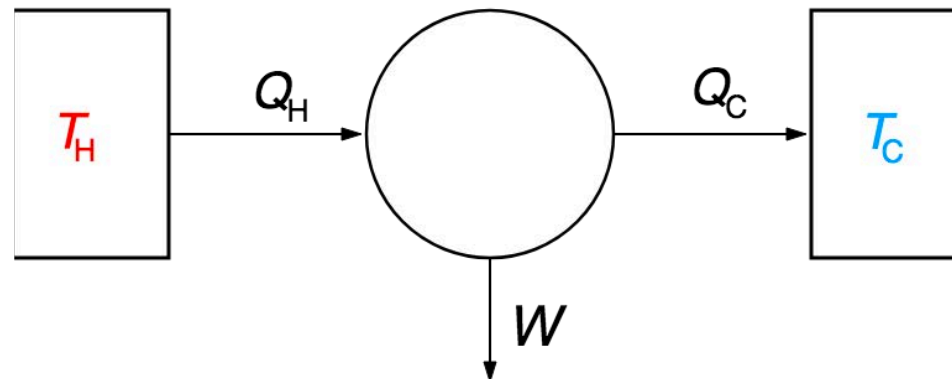
Tim Johnson, THERMOCALC short course, 2021

Thermodynamics:

The basis of the calculations

Thermodynamic basics

- **Thermodynamics** is the branch of physics relating heat with other forms of energy and how these affect matter
- It was formalised beginning in the late 18th century and the driving force behind the industrial revolution (how you can use **heat** to do **work**)
- Famous scientists that worked on it include Joule, Thomson (Lord Kelvin), Clausius, Maxwell and Boltzmann



A Carnot engine

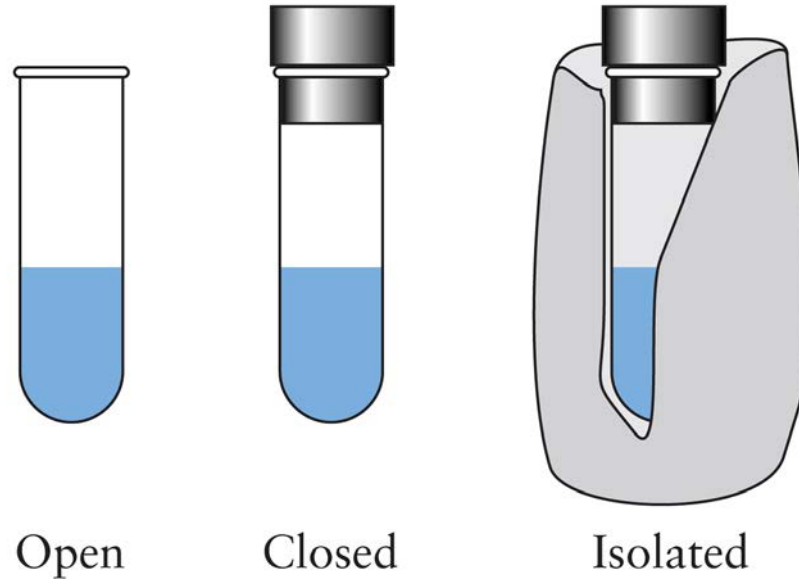
Thermodynamic basics – system

- A chemical system is some part of the universe that we wish to consider
- The system may be a planet, a layer within it (e.g. Earth's mantle), a magma chamber, a rock, a mineral grain or something else...



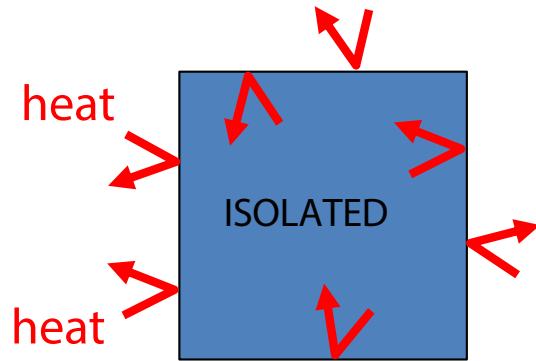
- Everything outside the system is the SURROUNDINGS
- Clearly the **bulk composition** (the average chemical composition) of a system depends on the size and nature of that system

Thermodynamic basics – system

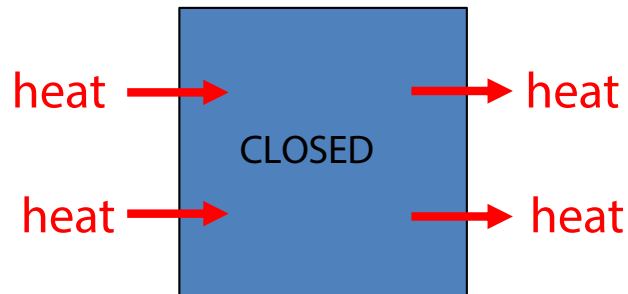


- A system can be **isolated** (nothing can flow in or out), **closed** (only energy can flow in or out) or **open** (energy and mass can flow in and out)

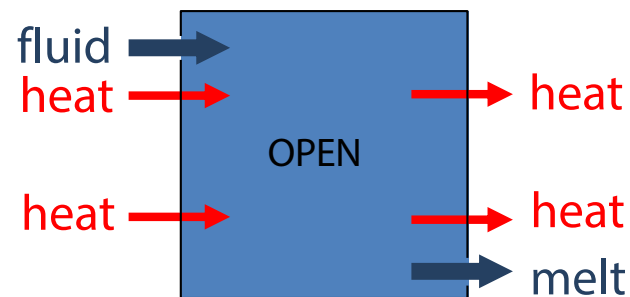
Thermodynamic basics – system



- **ISOLATED** systems cannot exchange energy or matter with their surroundings (unlikely in metamorphism)

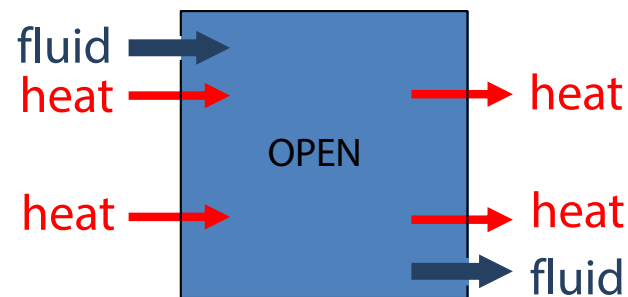
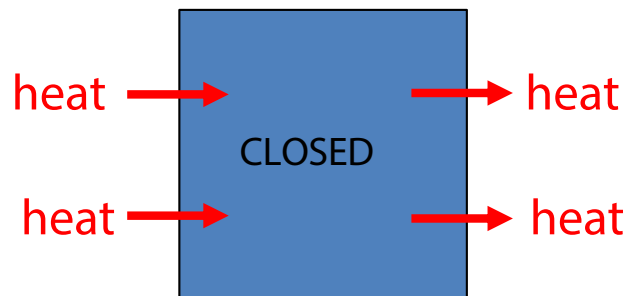
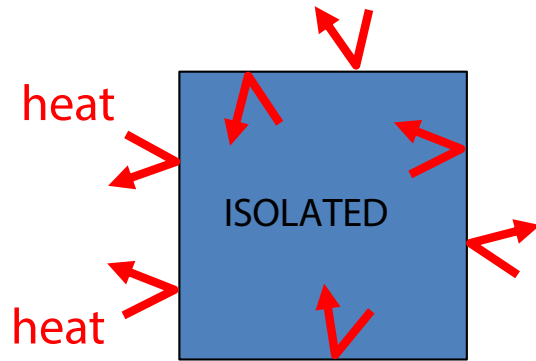


- **CLOSED** systems exchange energy but not matter with their surroundings (rock with no fluid flow in or out)



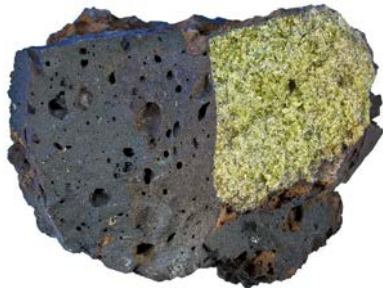
- **OPEN** systems exchange energy and matter with the surroundings (e.g. the rock is open to fluid flow, or melt loss)

Thermodynamic basics – system



- Most rocks are **open systems** during metamorphism, but chemical analyses show that the only significant chemical change in most rocks is loss or gain of H_2O and/or CO_2 (*unless/until they melt...*)
- Loss or gain of other chemical species, or METASOMATISM, is relatively rare (we will mostly ignore it)
- So most metamorphic rocks behave as a **closed system** (ignoring changes in $\text{H}_2\text{O}/\text{CO}_2$) and have bulk compositions unchanged from their **protolith**

Thermodynamic basics – system



Wide range of possible **protoliths**:

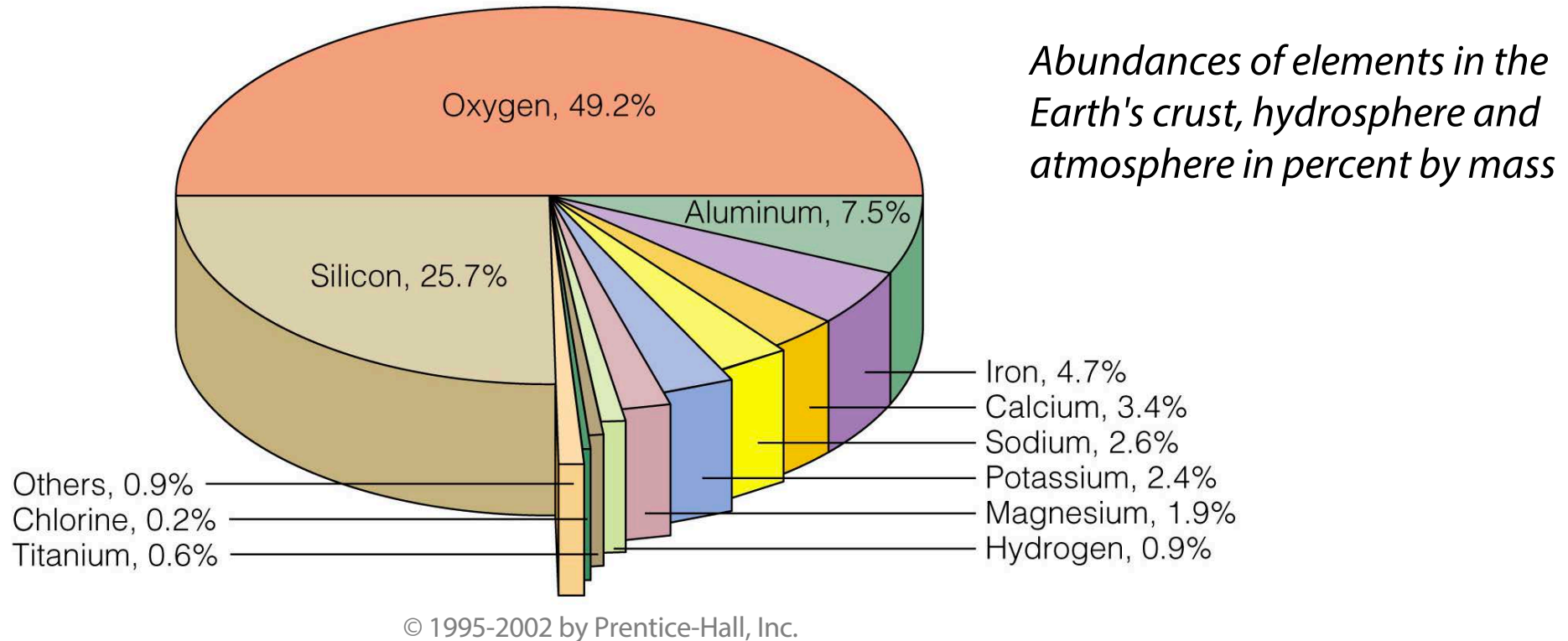
- Quartz-rich sandstone
- Greywacke
- Mudstone
- Marl
- Limestone
- Evaporite
- Ironstone
- Granite/rhyolite
- Gabbro/basalt
- Peridotite...

Thermodynamic basics – component



- A **component** is a chemically-independent constituent of a system.
- The number of components represents the minimum number of independent species (the 'ingredients') requires to define the composition of all **phases** of the system.
- Although there are 94 stable elements of Earth, most are very rare...

Thermodynamic basics – component



- For our purposes, the most important components (or 'ingredients') are the ten 'major' elements O, Si, Al, Fe, Mg, Ca, Na, K, H, Ti
- These are normally expressed as oxides (e.g. SiO_2 , TiO_2 , Al_2O_3 , etc.)
- Others minor/trace elements can be VERY important (later)...

Thermodynamic basics – protoliths



Oxide	A	B	C	D	E	F	G
SiO ₂	42.3	49.2	71.3	5.2	94.4	62.4	44.3
TiO ₂	0.6	1.8	0.3	0.1	0.1	1.1	0.1
Al ₂ O ₃	4.2	15.7	14.3	0.8	1.1	16.6	0.9
Fe ₂ O ₃	3.6	3.8	1.2	0.3	0.4	3.2	29.2
FeO	6.6	7.1	1.6	0.2	0.2	2.1	13.4
MnO	0.4	0.2	0.1	0.1	0.1	0.1	0.2
MgO	31.2	6.7	0.7	7.9	0.1	2.5	2.3
CaO	5.1	9.5	1.8	42.6	1.6	1.7	1.8
Na ₂ O	0.5	2.9	3.7	0.1	0.1	0.9	0.5
K ₂ O	0.3	1.1	4.1	0.3	0.2	3.0	1.3
H ₂ O	3.9	1.0	0.6	0.7	0.3	5.2	0.6
CO ₂	0.3	0.1	0.1	41.6	1.1	1.0	4.6
Total	99.0	99.1	99.8	99.9	99.7	99.8	99.2

- Peridotite (A)
- Gabbro (B)
- Granite (C)
- Limestone (D)
- Sandstone (E)
- Mudstone (F)
- Ironstone (G)



Thermodynamic basics – phase



- A **phase** is a material that is chemically homogeneous*, physically distinct, and (often) mechanically separable
- For our purposes, a **phase** is a **mineral**, a **fluid** (volatile phase) or a **melt**

* Solid solutions minerals are phases but, strictly speaking, zoned minerals are not...

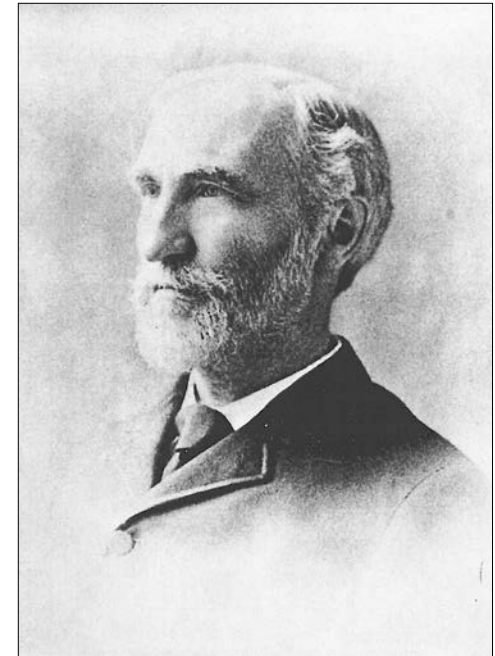


Thermodynamic basics - variance

*Gibbs phase rule: FOR A SYSTEM IN **EQUILIBRIUM***

$$F = C - P + 2$$

- F = degrees of freedom or **variance**; C = number of components, P = number of phases
- Variance is the number of independent variables you can change (e.g. P , T) without 'upsetting' the system
- Lower variance means more phases
- In large systems, low-variance regions are where the bulk of the (re)action takes place

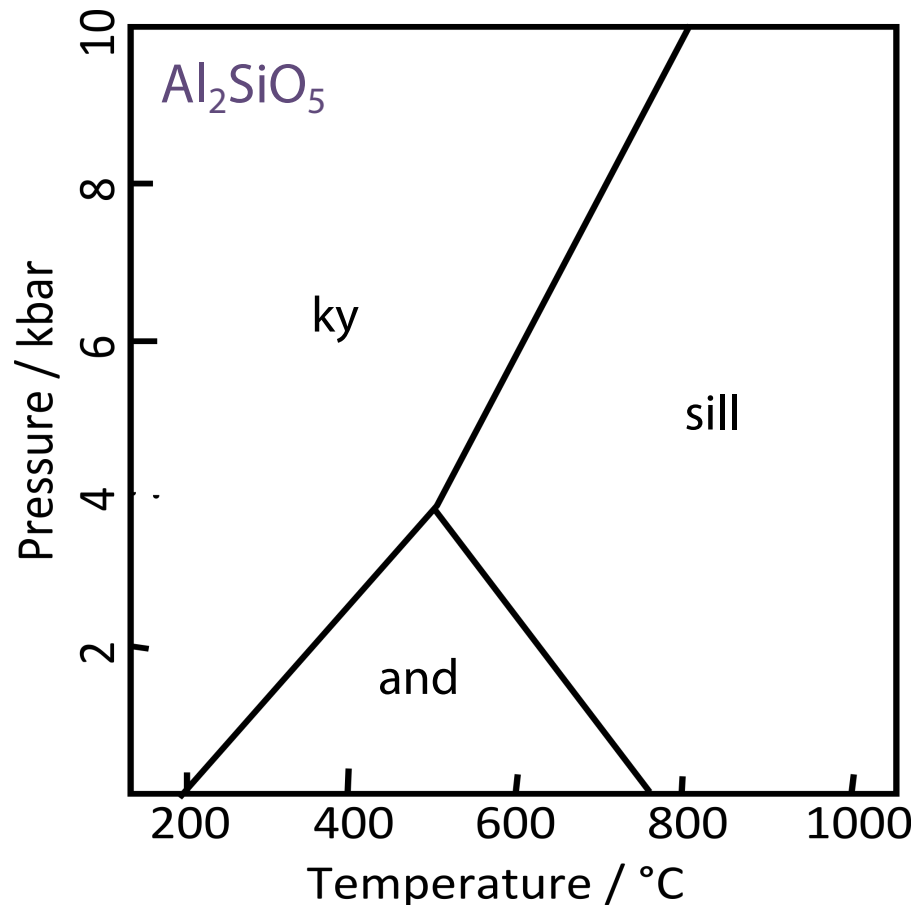


Josiah Willard Gibbs (1839–1909)

Thermodynamic basics - variance

Gibbs phase rule: FOR A SYSTEM IN **EQUILIBRIUM**

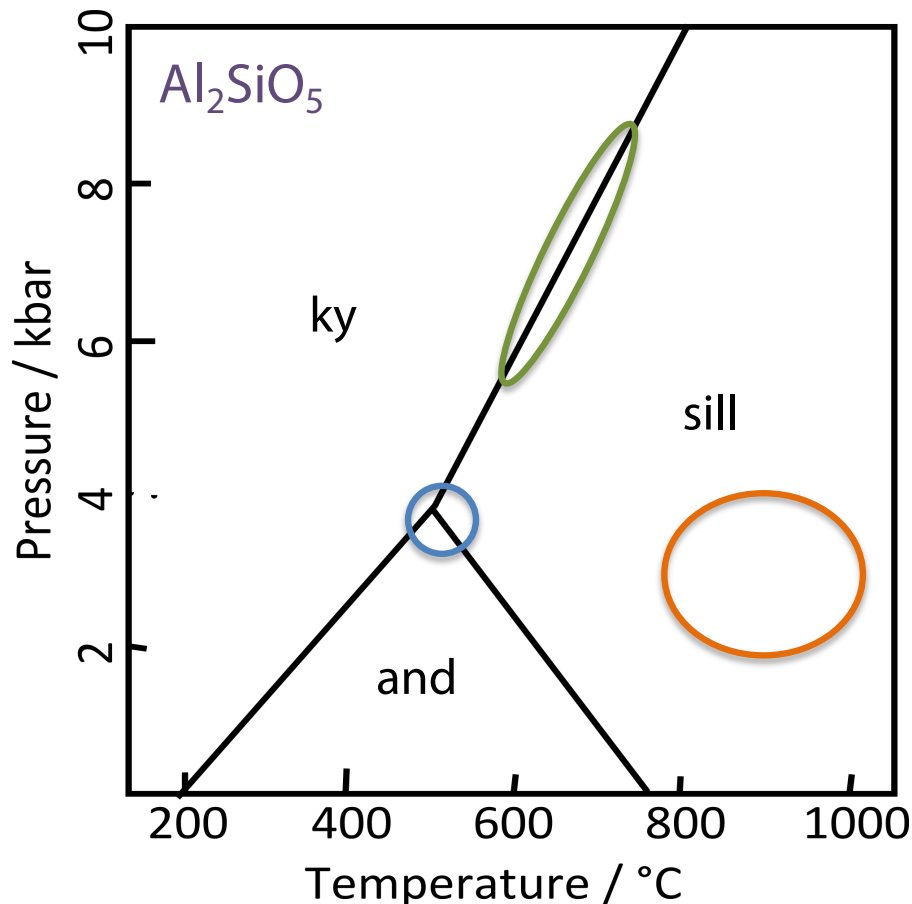
$$F = C - P + 2$$



Thermodynamic basics - variance

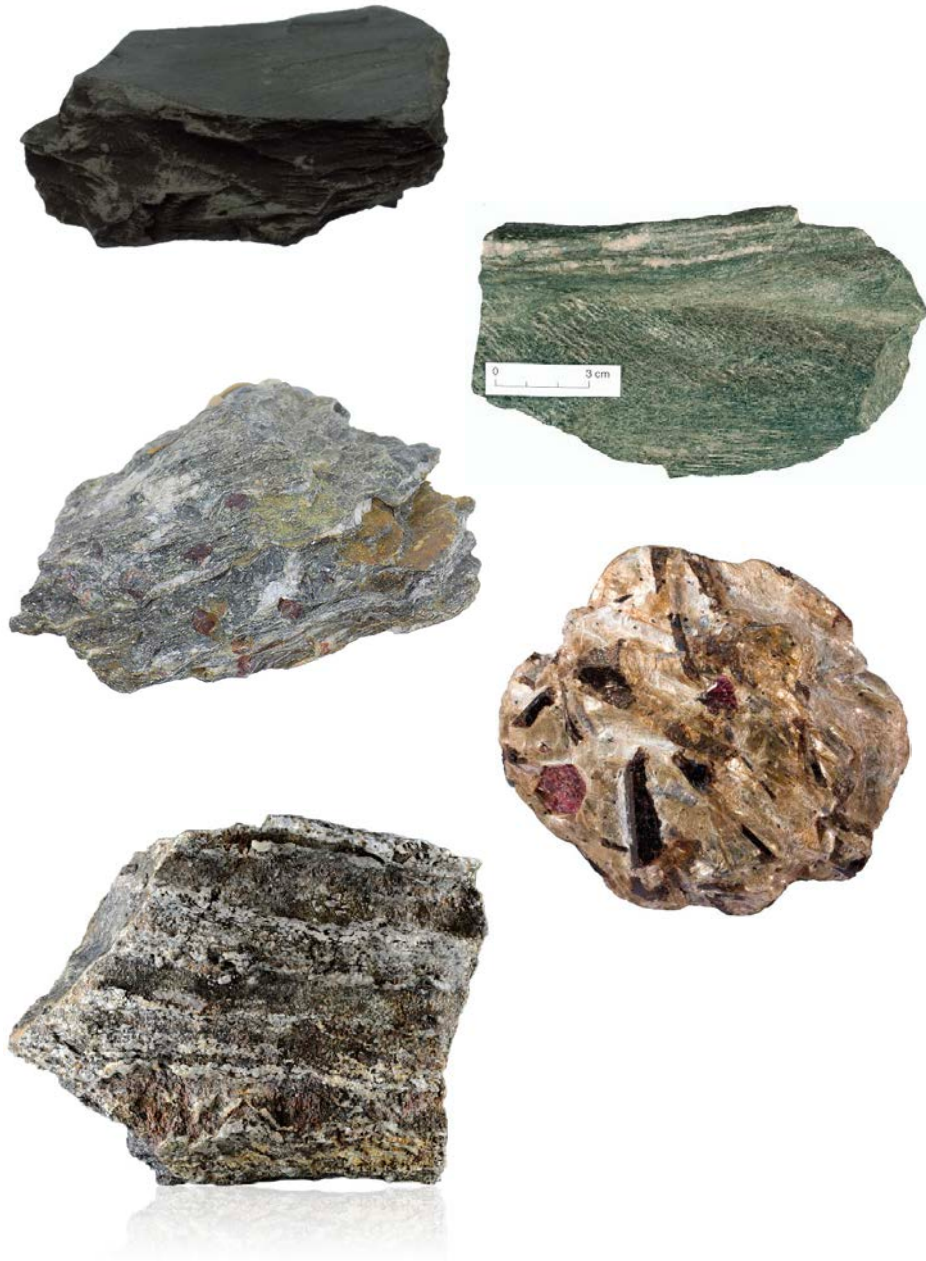
Gibbs phase rule: FOR A SYSTEM IN **EQUILIBRIUM**

$$F = C - P + 2$$



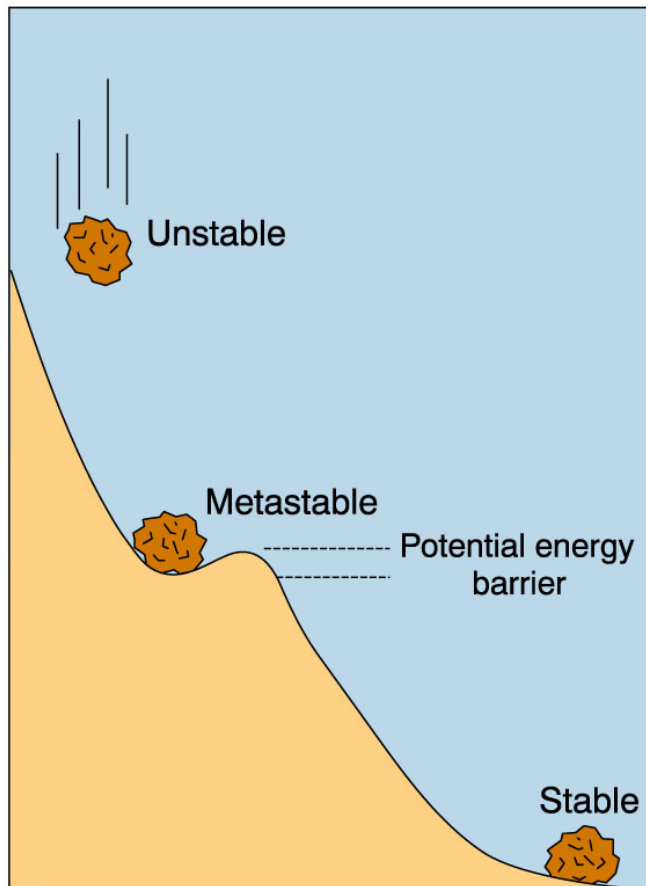
- At an **INVARIANT POINT** you can change neither P or T ($F = 0$) without upsetting the system
- On a **UNIVARIANT LINE** you can change either P OR T ($F = 1$), but not both, without upsetting the system = *discontinuous reaction*)
- In a **DIVARIANT FIELD** you can change both P AND T = *continuous reaction*

Thermodynamic basics – equilibrium



- Observation tells us that rocks of similar bulk composition but different metamorphic grade contain different minerals
- The rock undergo **reactions** in an attempt to achieve **equilibrium**
- The driver for these reactions are mainly changes in P and T that set up transient gradients in **chemical potential** (μ)
- The mechanism to flatten the chemical potentials (= equilibrium) is **DIFFUSION**

Thermodynamic basics – equilibrium



From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

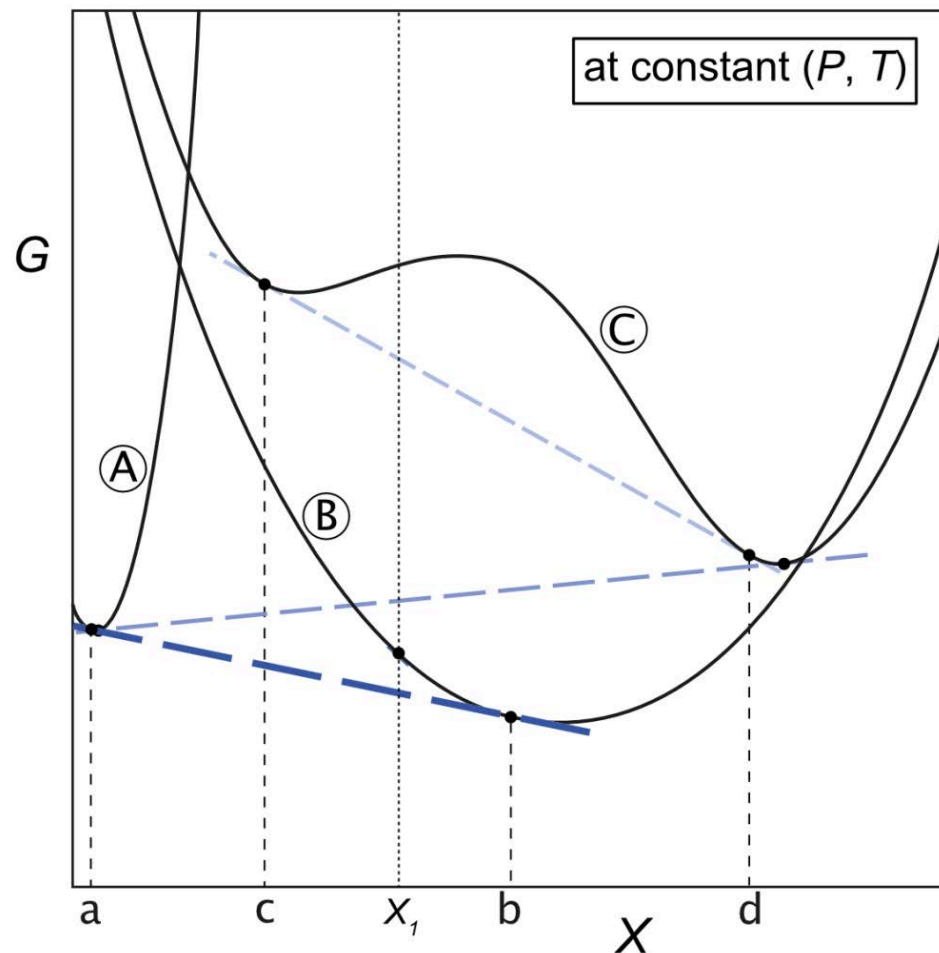
- A system can be stable, unstable or metastable
- We will only consider systems in **equilibrium**
- Equilibrium occurs when the macroscopic properties of a system do not change
- At equilibrium, the **chemical potential** (μ) of all components are flat (= no diffusion) and the composition of each phase is constant
- Practically speaking, it depends on the **scale** (in time and space) of the observation – **equilibrium volume**

Thermodynamic basics – equilibrium

- The **equilibrium volume** is that volume of the system that has reached equilibrium
- The phases that develop within the equilibrium volume will be a function of P , T and the bulk composition of the equilibrium volume
- A larger equilibrium volume is favoured by high T and the presence of fluids (melts or volatiles) that lead to large diffusional length scales



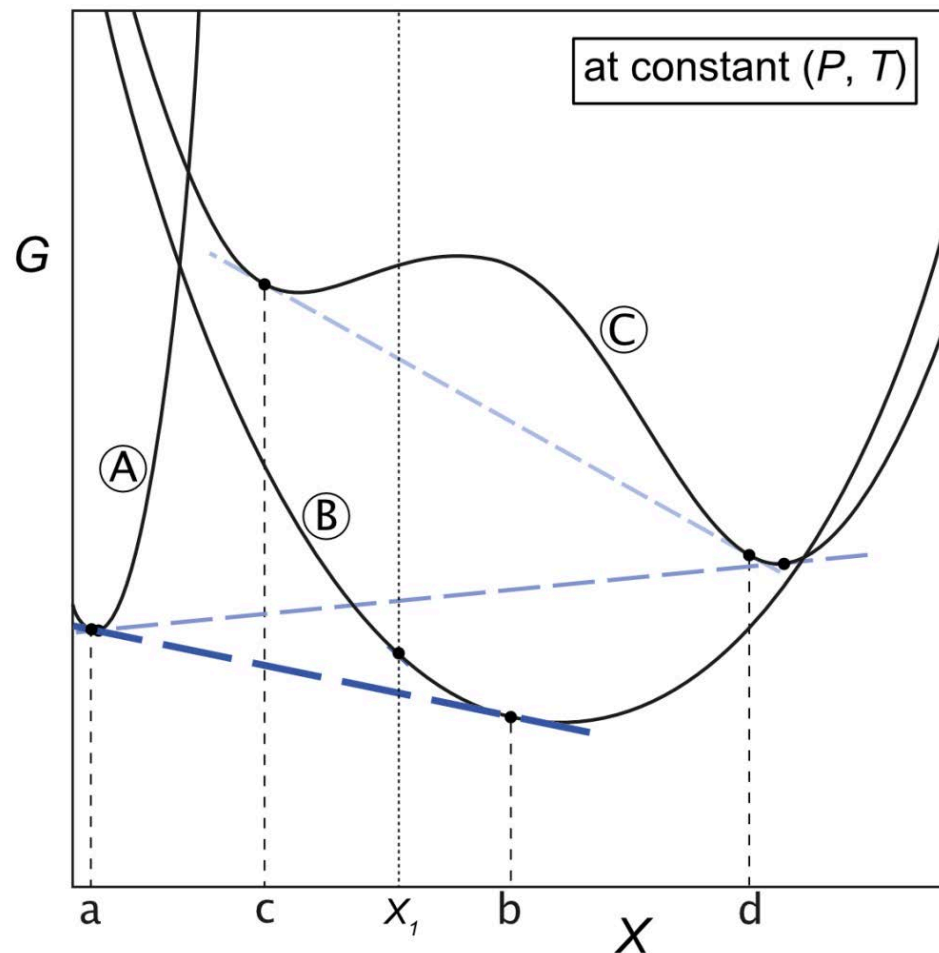
Thermodynamic basics – equilibrium



- G-X (Gibbs free energy – composition) diagram at constant P, T for phases A, B and C (phase C exhibits a solvus at intermediate compositions). Blue dashed common tangents indicate equilibria between phases that could be mass-balanced at bulk composition x_1 ; black dots indicate equilibrium compositions.

<https://hpxeosandthermocalc.org/the-hpx-eos/>

Thermodynamic basics – equilibrium



- The most stable assemblage that could form in rock X_1 is coexisting phase A with composition a and phase B with composition b (dark blue tangent).
- The next most stable assemblage is pure phase B with composition X_1 , followed by coexisting A and C (mid-blue tangent), followed by two coexisting phases of C's structure and compositions c and d (light blue tangent).

<https://hpxeosandthermocalc.org/the-hpx-eos/>

Thermodynamic basics – reactions

3 anorthite \rightarrow grossular + 2 kyanite + quartz



- As P – T conditions change, rocks **equilibrate** by undergoing **reaction**
- Reactions involve phases that are consumed (= **REACTANTS**; left-hand-side) and phases that are produced (= **PRODUCTS**; right hand side)
- To consume mass (as we must), reactions must be **BALANCED** (= equal number of moles of components on each side of the reaction)
- Balancing is achieved using **STOICHIOMETRIC COEFFICIENTS**

Thermodynamic basics – equilibrium

$$0 = \Delta G + RT \ln K$$

- ΔG = Gibbs free energy of the reaction between **pure end-members**
- K = equilibrium constant in terms of end-member activities
- T = temperature
- R = gas constant

Thermodynamic basics – end-member data

In a 'simple' form:

$$G = E + PV - TS$$

- E = internal energy (total energy)
- S = entropy (degree of disorder or 'randomness')
- V = volume
- T = temperature
- P = pressure

Thermodynamic basics – end-member data

In a 'simple' form:

$$G = H - TS$$

- H = enthalpy (energy associated with expansion/contraction)
- S = entropy (degree of disorder or 'randomness')
- V = volume
- T = temperature
- P = pressure

Thermodynamic basics – end-member data

For REACTIONS:

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

- E = internal energy (total energy)
- S = entropy (degree of disorder or 'randomness')
- V = volume
- T = temperature
- P = pressure

Thermodynamic basics – end-member data

In a 'simple' form:

$$\Delta G = \Delta H - T\Delta S$$

- H = enthalpy (energy associated with expansion/contraction)
- S = entropy (degree of disorder or 'randomness')
- V = volume
- T = temperature
- P = pressure

Thermodynamic basics – end-member data

In a less simple form:

$$\Delta G = \Delta H - T\Delta S + \int_{298}^T C_p dT - \int_{298}^T \frac{C_p}{T} dT + P\Delta V \left(1 + \alpha(T - 298) - \frac{\beta P}{2} \right)$$

The important point is that all these thermodynamic data are well understood and contained within the data set....

Thermodynamic basics – end-member data

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Table 2a. Molar thermodynamic properties (units: kJ, K, kbar) of the end-members whose formulae can be found in Table 1.

Group	End-member	$\Delta_f H$	$\sigma(\Delta_f H)$	S	V	C_P				$\alpha\kappa$				ℓ
						a	b	c	d	α_0	κ_0	κ'_0	κ''_0	
Garnet and olivine	Almandine (alm)	−5260.65	1.31	342.00	11.525	0.6773	0	−3772.7	−5.0440	2.12	1900.0	2.98	−0.0016	1
	Andradite (andr)	−5769.08	1.56	316.40	13.204	0.6386	0	−4955.1	−3.9892	2.86	1588.0	5.68	−0.0036	
	grossular (gr)	−6642.95	1.46	255.00	12.535	0.6260	0	−5779.2	−4.0029	2.20	1720.0	5.53	−0.0032	
	Knorringite (knor)	−5687.75	3.88	317.00	11.738	0.6130	0.3606	−4178.0	−3.7294	2.37	1743.0	4.05	−0.0023	
	Majorite (maj)	−6050.33	9.62	255.20	11.457	0.7136	−0.0997	−1158.2	−6.6223	1.83	1600.0	4.56	−0.0028	
	Pyrope (py)	−6282.13	1.06	269.50	11.313	0.6335	0	−5196.1	−4.3152	2.37	1743.0	4.05	−0.0023	
	Spessartine (spss)	−5693.65	3.14	335.30	11.792	0.6469	0	−4525.8	−4.4528	2.27	1740.0	6.68	−0.0038	
	Clinohumite (chum)	−9609.82	2.49	443.00	19.785	1.0700	−1.6533	−7899.6	−7.3739	2.91	1194.0	4.79	−0.0040	
	Fayalite (fa)	−1477.74	0.68	151.00	4.631	0.2011	1.7330	−1960.6	−0.9009	2.82	1256.0	4.68	−0.0037	
	Forsterite (fo)	−2172.57	0.57	95.10	4.366	0.2333	0.1494	−603.8	−1.8697	2.85	1285.0	3.84	−0.0030	
	Larnite (lrn)	−2307.04	0.90	127.60	5.160	0.2475	−0.3206	0	−2.0519	2.90	985.0	4.07	−0.0041	
	Monticellite (mont)	−2251.31	0.52	109.50	5.148	0.2507	−1.0433	−797.2	−1.9961	2.87	1134.0	3.87	−0.0034	
	Tephroite (teph)	−1733.95	1.05	155.90	4.899	0.2196	0	−1292.7	−1.3083	2.86	1256.0	4.68	−0.0037	
Aluminosilicates	Andalusite (and)	−2588.72	0.68	92.70	5.153	0.2773	−0.6588	−1914.1	−2.2656	1.81	1442.0	6.89	−0.0048	2
	Kyanite (ky)	−2593.02	0.67	83.50	4.414	0.2794	−0.7124	−2055.6	−2.2894	1.92	1601.0	4.05	−0.0025	
	Sillimanite (sill)	−2585.85	0.68	95.40	4.986	0.2802	−0.6900	−1375.7	−2.3994	1.12	1640.0	5.06	−0.0031	
	Mullite (amul)	−2485.51	0.91	113.00	5.083	0.2448	0.0968	−2533.3	−1.6416	1.36	1740.0	4.00	−0.0023	
	Mullite (smul)	−2569.28	0.69	101.50	4.987	0.2802	−0.6900	−1375.7	−2.3994	1.36	1740.0	4.00	−0.0023	
	Chloritoid (fctd)	−3208.31	0.80	167.00	6.980	0.4161	−0.3477	−2835.9	−3.3603	2.80	1456.0	4.06	−0.0028	
	Chloritoid (mctd)	−3549.31	0.75	146.00	6.875	0.4174	−0.3771	−2920.6	−3.4178	2.63	1456.0	4.06	−0.0028	
	Chloritoid (mnctd)	−3336.20	1.68	166.00	7.175	0.4644	−1.2654	−1147.2	−4.3410	2.60	1456.0	4.06	−0.0028	
	Staurolite (fst)	−23 755.04	6.34	1010.00	44.880	2.8800	−5.6595	−10642.0	−25.3730	1.83	1800.0	4.76	−0.0026	
	Staurolite (mnst)	−24 246.42	8.60	1034.00	45.460	2.8733	−8.9064	−12688.0	−24.7490	2.09	1800.0	4.76	−0.0026	
	Staurolite (mst)	−25 124.32	6.28	910.00	44.260	2.8205	−5.9366	−13774.0	−24.1260	1.81	1684.0	4.05	−0.0024	
	Topaz (tpz)	−2900.76	0.96	100.50	5.339	0.3877	−0.7120	−857.2	−3.7442	1.57	1315.0	4.06	−0.0031	

From Holland & Powell (2011)

Thermodynamic basics – equilibrium

$$0 = \Delta G + RT \ln K$$

- ΔG° = Gibbs free energy of the reaction between pure end-members
- K = equilibrium constant in terms **end-member activities in the phase**
- T = temperature
- R = gas constant

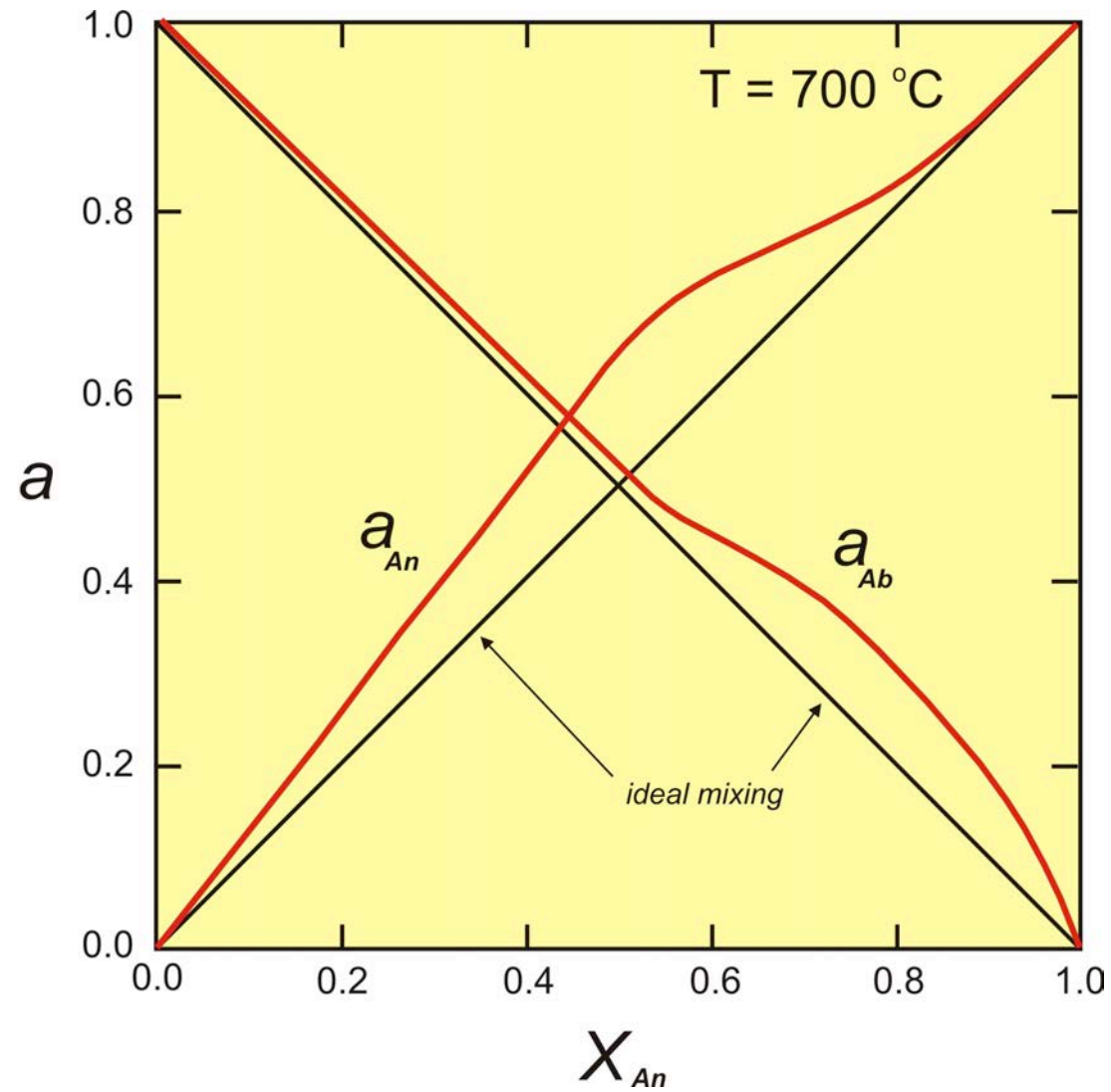
Thermodynamic basics – solid-solutions

For a balanced chemical reaction between end members: $A + 2B = 3X + 4Y$,

$$K = \frac{a_X^3 \cdot a_Y^4}{a_A \cdot a_B^2}$$

- We can think of **activity**, a , as the 'effective' concentration
- For reactions between pure minerals, $a = 1$ so $K = 0$. For solid solutions (most minerals) $a \neq 1$, and $K \neq 0$
- Activity is some (commonly complex) function of the actual concentration (mole fraction, X) of a component
- This function (activity–composition, or a – X , relationship) is part of the **solution models** (e.g. White *et al.* 2014a,b)

Thermodynamic basics – solid-solutions



Thermodynamic basics – requirements satisfied

$$0 = \Delta G^{\circ} + RT \ln K$$

end-member data

solution models

Journal of
METAMORPHIC GEOLOGY

J. metamorphic Geol., 2011, **29**, 333–383 doi:10.1111/j.1525-1314.2010.00923.x

An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids

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²School of Earth Sciences, The University of Melbourne, Victoria 3010, Australia (powell@unimelb.edu.au)

ABSTRACT The thermodynamic properties of 254 end-members, including 210 mineral end-members, 18 silicate liquid end-members and 26 aqueous fluid species are presented in a revised and updated internally consistent thermodynamic data set. The *PVT* properties of the data set phases are now based on a modified Tait equation of state (EOS) for the solids and the Pitzer & Sterner (1995) equation for gaseous components. Thermal expansion and compressibility are linked within the modified Tait EOS (TEOS) by a thermal pressure formulation using an Einstein temperature to model the temperature dependence of both the thermal expansion and bulk modulus in a consistent way. The new EOS has led to improved fitting of the phase equilibrium experiments. Many new end-members have been added, including several deep mantle phases and, for the first time, sulphur-bearing minerals. Silicate liquid end-members are in good agreement with both phase equilibrium experiments and measured heat of melting. The new dataset considerably enhances the capabilities for thermodynamic calculation on rocks, melts and aqueous fluids under crustal to deep mantle conditions. Implementations are already available in THERMOCALC to take advantage of the new data set and its methodologies, as illustrated by example calculations on sapphirine-bearing equilibria, sulphur-bearing equilibria and calculations to 300 kbar and 2000 °C to extend to lower mantle conditions.

Key words: equation of state; internally consistent dataset; thermodynamic data.

Holland & Powell (2011)

Journal of
METAMORPHIC GEOLOGY

J. metamorphic Geol., 2014, **32**, 261–286 doi:10.1111/jmg.12071

New mineral activity–composition relations for thermodynamic calculations in metapelitic systems

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ABSTRACT New activity–composition (*a*–*x*) relations for minerals commonly occurring in metapelites are presented for use with the internally consistent thermodynamic dataset of Holland & Powell (2011, *Journal of Metamorphic Geology*, **29**, 333–383). The *a*–*x* relations include a broader consideration of Fe₂O₃ in minerals, changes to the formalism of several phases and order-disorder in all ferromagnesian minerals where Fe–Mg mixing occurs on multiple sites. The *a*–*x* relations for chlorite, biotite, garnet, chloritoid, staurolite, cordierite, orthopyroxene, muscovite, paragonite and margarite have been substantially reparameterized using the approach outlined in the companion paper in this issue. For the first time, the entire set of *a*–*x* relations for the common ferromagnesian minerals in metapelitic rocks is parameterized simultaneously, with attention paid to ensuring that they can be used together to calculate phase diagrams of geologically appropriate topology. The *a*–*x* relations developed are for use in the Na₂O–CaO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O–TiO₂–O₂ (NCKFMASHTO) system for both subsolidus and suprasolidus conditions. Petrogenetic grids in KFMASH and KFMASHTO are similar in topology to those produced with earlier end-member datasets and *a*–*x* relations, but with some notable differences. In particular, in subsolidus equilibria, the FeO/(FeO + MgO) of garnet is now greater than in coexisting staurolite, bringing a number of key staurolite-bearing equilibria into better agreement with inferences from field and petrographic observations. Furthermore, the addition of Fe³⁺ and Ti to a number of silicate phases allows more plausible equilibria to be calculated in relevant systems. Pseudosections calculated with the new *a*–*x* relations are also topologically similar to equivalent diagrams using earlier *a*–*x* relations, although with many low variance fields shifting in *P*–*T* space to somewhat lower pressure conditions.

Key words: *a*–*x* relations; metapelite; NCKFMASHTO; pseudosection; THERMOCALC.

White et al. (2014a)

The main tools:

Take your pick

Methods of calculation – the main players

Perple_**x**

Connolly (2009)



Powell & Holland (1988)



de Capitani & Petrakakis (2010)

- All are (sophisticated) tools that rely on end-member data, solution models and data input by the user
- Perple_X and Theriak-Domino are Gibbs free energy minimizers – they should automatically find the stable assemblage
- THERMOCALC uses an algorithm to solve non-linear equations – it has no 'idea' what the equilibrium (lowest G) assemblage is
- As/if they use the same input, they should produce the same diagrams

Methods of calculation – the main players

Perple_X

<http://www.perplex.ethz.ch/>

- Very easy to use (this has positive and negative connotations)
- Calculations can take a long time, but can be hugely speeded up by using Paralyzer, a Matlab script written by Mark Caddick (Virginia Tech.)
- Diagrams contoured easily for other rock properties (abundance and composition of minerals, V , S , ρ , seismic velocity, etc...)
- Perple_X produces (to me) aesthetically-challenged diagrams

Methods of calculation – the main players



<https://titan.minpet.unibas.ch/minpet/theriak/theruser.html>

- Very easy to use (this has positive and negative connotations)
- Can also be used to extract other useful rock information
- Lags behind somewhat with updates (e.g. no hp ds6 models yet)
- Produces aesthetically pleasing diagrams of publication standard
- I have limited experience but what I have heard is all very positive

Methods of calculation – the main players



<https://hpxeosandthermocalc.org/>

- Much more challenging to use (with positive and negative connotations)
- Used to be painful to contour diagrams, but this is being solved (see also the TCInvestigator GUI by Pearce *et al.* (2015))
- With some exceptions (the abundance and composition of minerals, activities), extracting other useful rock properties in the format (in terms of variables) you might desire is non-trivial, but this is also changing
- My program of choice for anybody learning phase equilibrium modelling

Danger!



- The largest uncertainties in phase equilibrium modelling derive from the user
- Take care in the selection and calculation of bulk composition – they involve educated guesswork
- For Perple_X and Theriak Domino, take EXTRA care in your choice of solution models
- In the end, the models are models. DO NOT OVER-INTERPRET THE RESULTS!

Danger!



- Phase equilibrium is very powerful, but is useless without:
 - CAREFUL FIELD AND PETROGRAPHIC OBSERVATIONS
 - COLLECTING AND ANALYSING APPROPRIATE ROCKS
 - **THOUGHT**

*What types of rocks can I
model?*

From the top of the crust to the deep mantle

Partial melting – solution models

New mineral activity–composition relations for thermodynamic calculations in metapelitic systems

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Key words: *a*–*x* relations; metapelite; NCKFMASHTO; pseudosection; THERMOCALC.

INTRODUCTION

Quantitative phase petrology has developed over the last decades into a widely used approach for understanding the evolution of metamorphic rocks and for deriving *P*–*T* information. Such progress has been firmly rooted in the development of better thermodynamic data for the end-members of minerals, fluid and melt, improved and extended activity–composition (*a*–*x*) relations for minerals and the improvement of software to undertake calculations. Using these tools, metamorphic petrologists have increased understanding of many metamorphic processes and placed better quantitative constraints on the conditions of formation of metamorphic rocks. Despite this progress, there remain many limitations and sources of uncertainty in the approach. In particular, it is the lack of, or limits on, the *a*–*x* relations that currently represents the greatest constraint on the efficacy of the approach. Existing sets of *a*–*x* relations of minerals (e.g. White

et al., 2001 2007; Diener & Powell, 2012) were built up over more than a decade using a range of approaches, different dataset versions and different *a*–*x* relations for the other minerals involved. This has resulted in inherent inconsistencies between the *a*–*x* relations for the different minerals of interest. This is reflected in calculated mineral compositions and mineral proportions being unreliable, even if fields in pseudosections can commonly be found to match those observed in rocks.

The release of the newly updated internally consistent thermodynamic dataset of Holland & Powell (2011) offers an opportunity for reparameterizing and substantially improving *a*–*x* relations. In fact, the previous family of *a*–*x* relations as used with the Holland & Powell (1998) dataset are not valid for use with the new dataset and must be replaced, for the following reasons: (i) An advance in dataset generation means that a wider range of experimental data involving solid solutions are used, requiring that parts

- Models permitting the quantitative investigation of partial melting of ‘pelitic’ systems (i.e. haplogranitic melts) have been around since 2000
- These were updated to work with the most recently available Holland & Powell (2011) end-member thermodynamic data in 2014.

Crustal protoliths



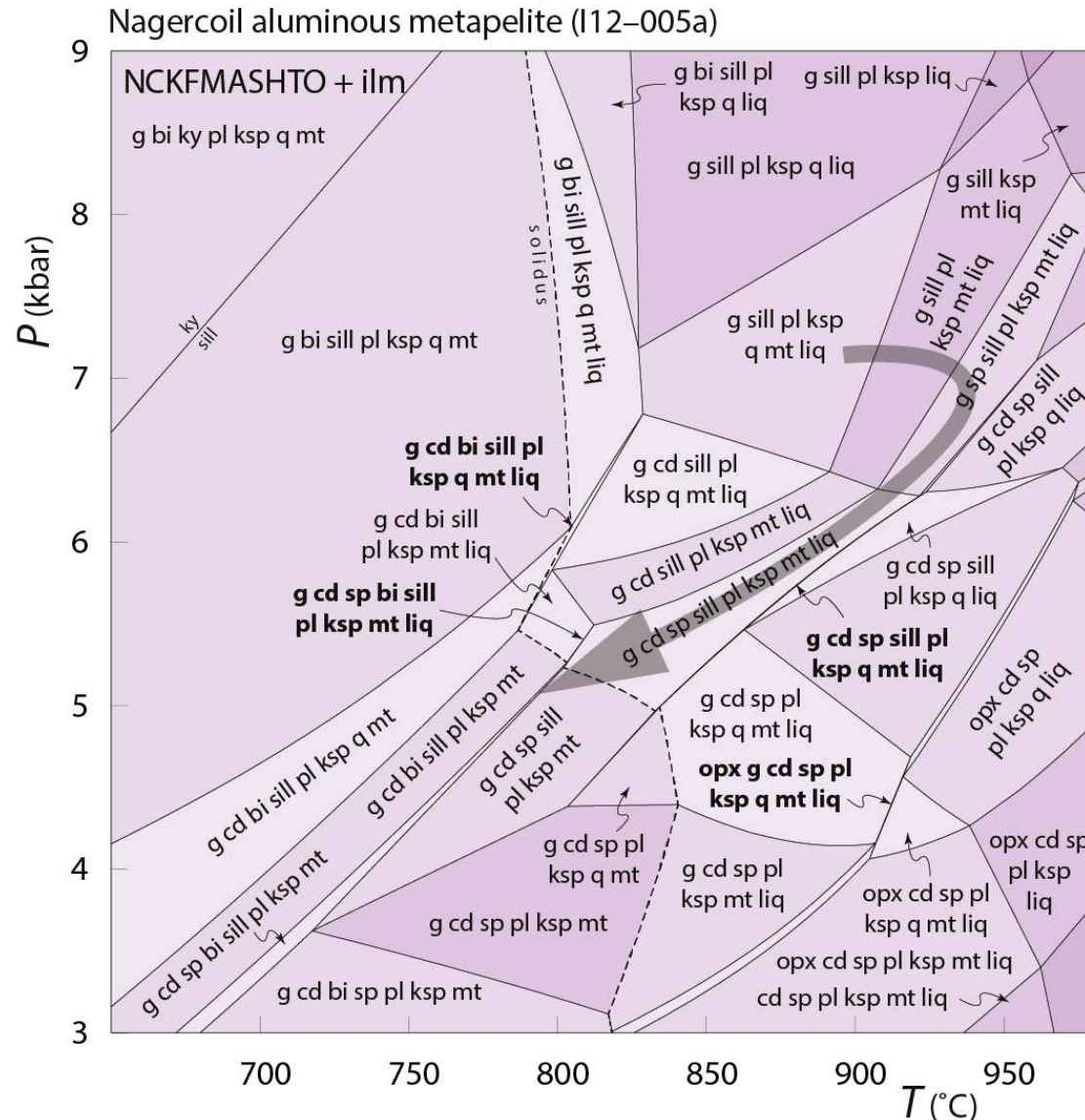
Zabriskie Point, Death Valley, USA © Brigitte Werner

Crustal protoliths



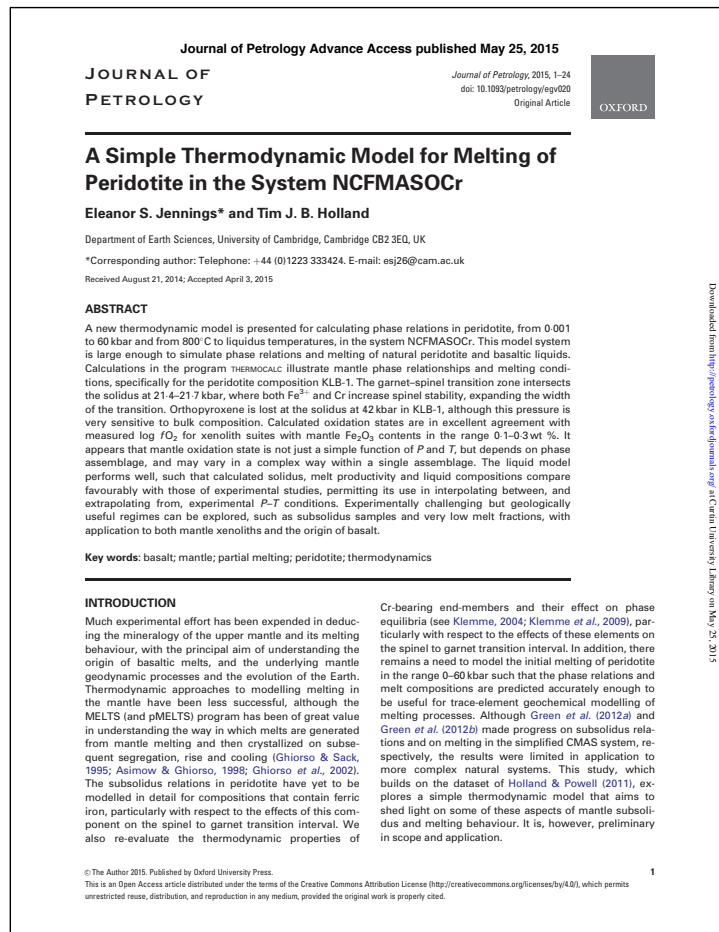
Cerro Torre (<http://www.summitpost.org/>)

Melting an aluminous metapelite



- NCKFMASHTO using White et al. (2014) solution models
- Using these models, we can make granite = evolved continental crust

Relatively recent 'game changers'



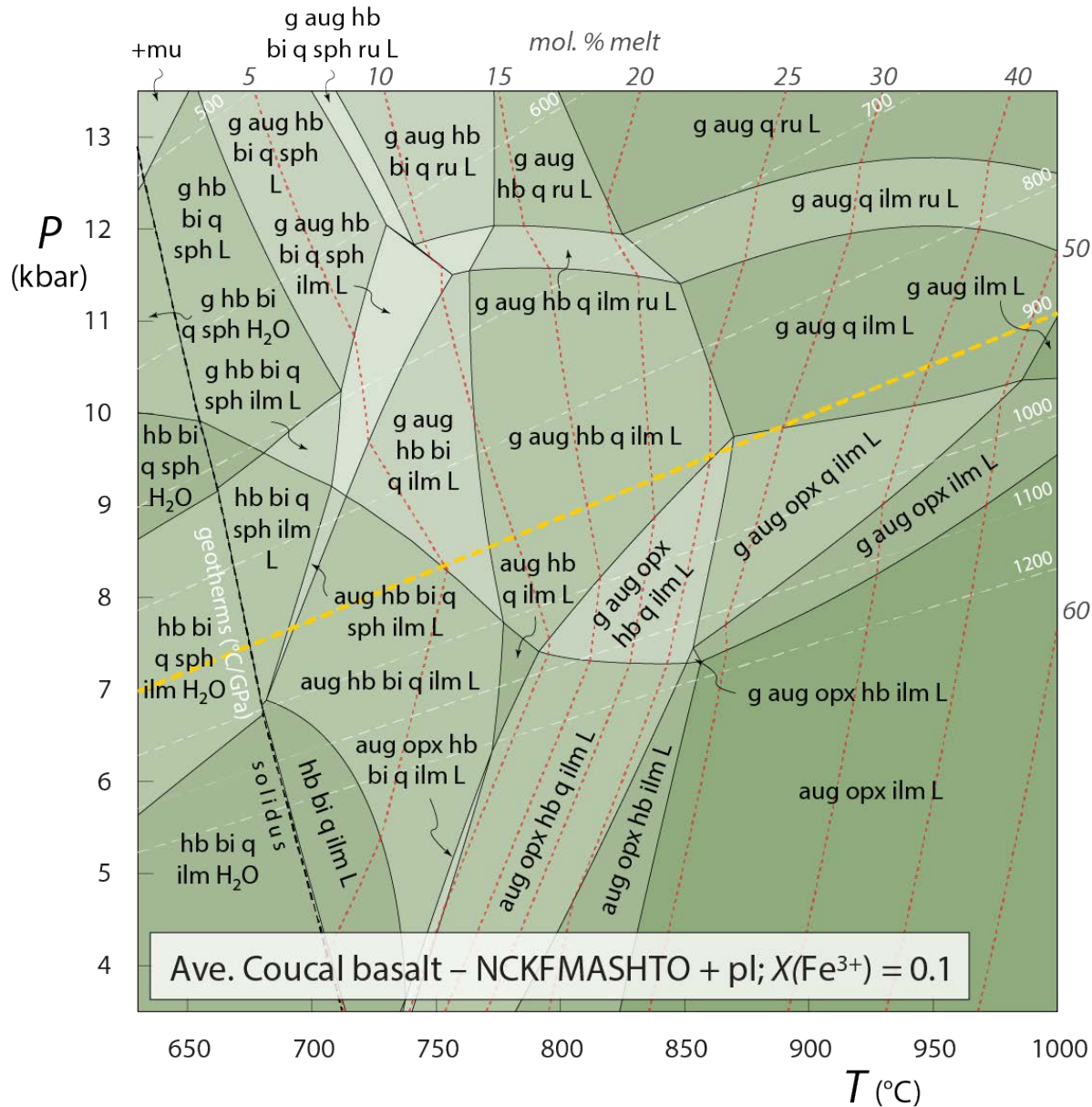
- Models permitting the quantitative investigation of partial melting of ultramafic and mafic systems appeared in 2015 and 2016, respectively
- These three systems work **INDEPENDENTLY** (the melt models are different)

Crustal protoliths



Cuillins, Skye (<http://www.worldfortravel.com/>)

Melting a Paleoarchaeean basalt



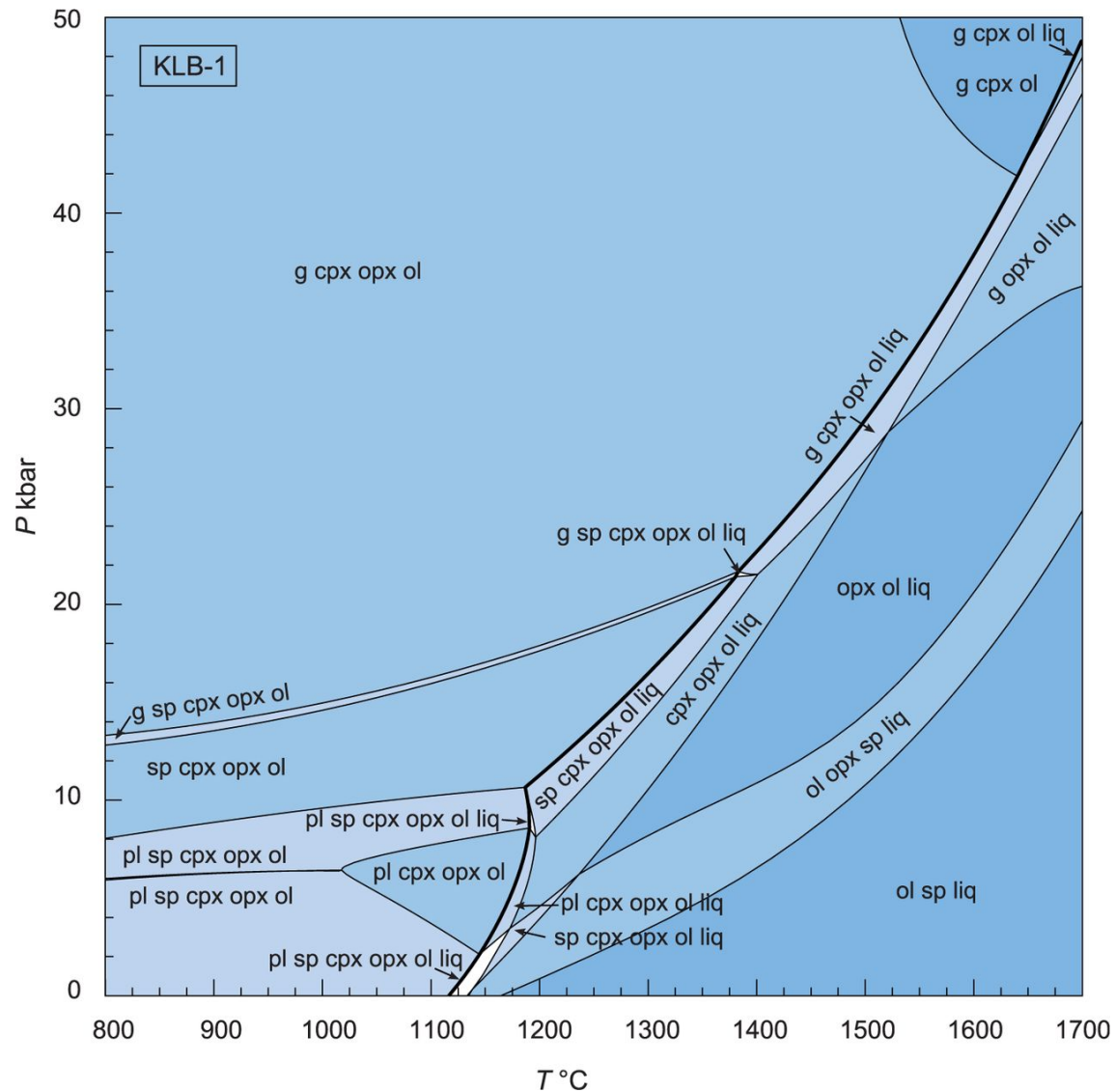
- NCKFMASHTO using Green et al. (2016) solution models
- Using these models, we can make tonalite and trondhjemite = primitive continental crust

Mantle protoliths



Mantle Peridotite, Samail Ophiolite, Oman © Evelyn Mervine

Melting the mantle



From Jennings & Holland (2015)

- Extends simple CMAS models (Green et al., 2012) into the NCFMASOCr system
- Using these models, we can make primary basaltic (oceanic) crust

A more recent 'game changer'

JOURNAL OF
PETROLOGY

Journal of Petrology, 2018, Vol. 59, No. 5, 881–900
doi: 10.1093/ptrology/egy048
Advance Access Publication Date: 16 May 2018
Original Article



Melting of Peridotites through to Granites: A Simple Thermodynamic Model in the System KNCFMASHTOCr

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ABSTRACT

A new set of thermodynamic models is presented for calculating phase relations in bulk compositions extending from peridotite to granite, from 0.001 to 70 kbar and from 650°C to peridotite liquidus temperatures, in the system $K_2O-Na_2O-CaO-FeO-MgO-Al_2O_3-SiO_2-H_2O-TiO_2-Fe_2O_3-Cr_2O_3$ (KNCFMASHTOCr). The models may be used to calculate phase equilibria in partial melting of a large range of mantle and crustal compositions. They provide a good fit to experimental phase relation topologies and melt compositions across the compositional range of the model. Compared with the preliminary model of Jennings, E. S. & Holland, T. J. B. (2015) (A simple thermodynamic model for melting of peridotite in the system NCFMASOcr. *Journal of Petrology* 56, 869–892) for peridotite–basalt melting relations, the inclusion of K_2O and TiO_2 allows for better modelling of small melt fractions in peridotite melting, and in reproducing rutile-bearing eclogite melting at high pressures. An improved order–disorder model for spinel is now incorporated. Above 10 kbar pressure, wet partial melting relations may be significantly affected by the dissolution of silicates in aqueous fluid, so the set of models includes an aqueous low-density silicate-bearing fluid in addition to a high-density H_2O -bearing silicate melt. Oxygen fugacity may be readily calculated for the whole range of bulk compositions investigated, and the effect of water content on melt fO_2 is assessed.

Key words: basalt; mantle; partial melting; peridotite; thermodynamics

INTRODUCTION

The modelling of melting relations in rock bulk compositions is an important goal in petrology. Modelling makes it possible to predict mineral + melt assemblages at pressures, temperatures and compositions where existing experimental data must be interpolated. Model predictions may even, with caution, be extrapolated to regimes where experimental constraints would be challenging or time-consuming to obtain. Partial melting plays a major role in both modulating and probing Earth processes, the former by advecting heat and matter, and the latter by influencing seismic velocities. Consequently, the capacity to make accurate predictions of partial melting relations has great significance for Earth system science.

In order to model partial melting, a thermodynamic description is needed for each of the phases involved. The silicate melt is perhaps the most difficult. This is fundamentally because there is no obvious way to write the entropy of the melt, unlike in a crystalline solid, for which the configurational entropy of cation mixing on lattice sites is well defined. However, the problem is exacerbated by the enormous extent of composition space that melts are able to occupy, relative to any solid solution. Thermodynamic modellers have previously handled this problem by modelling subsets of this potential composition space, relevant to melt in a limited range of settings.

Using this approach, partial melting can now be handled in a wide range of contexts using different

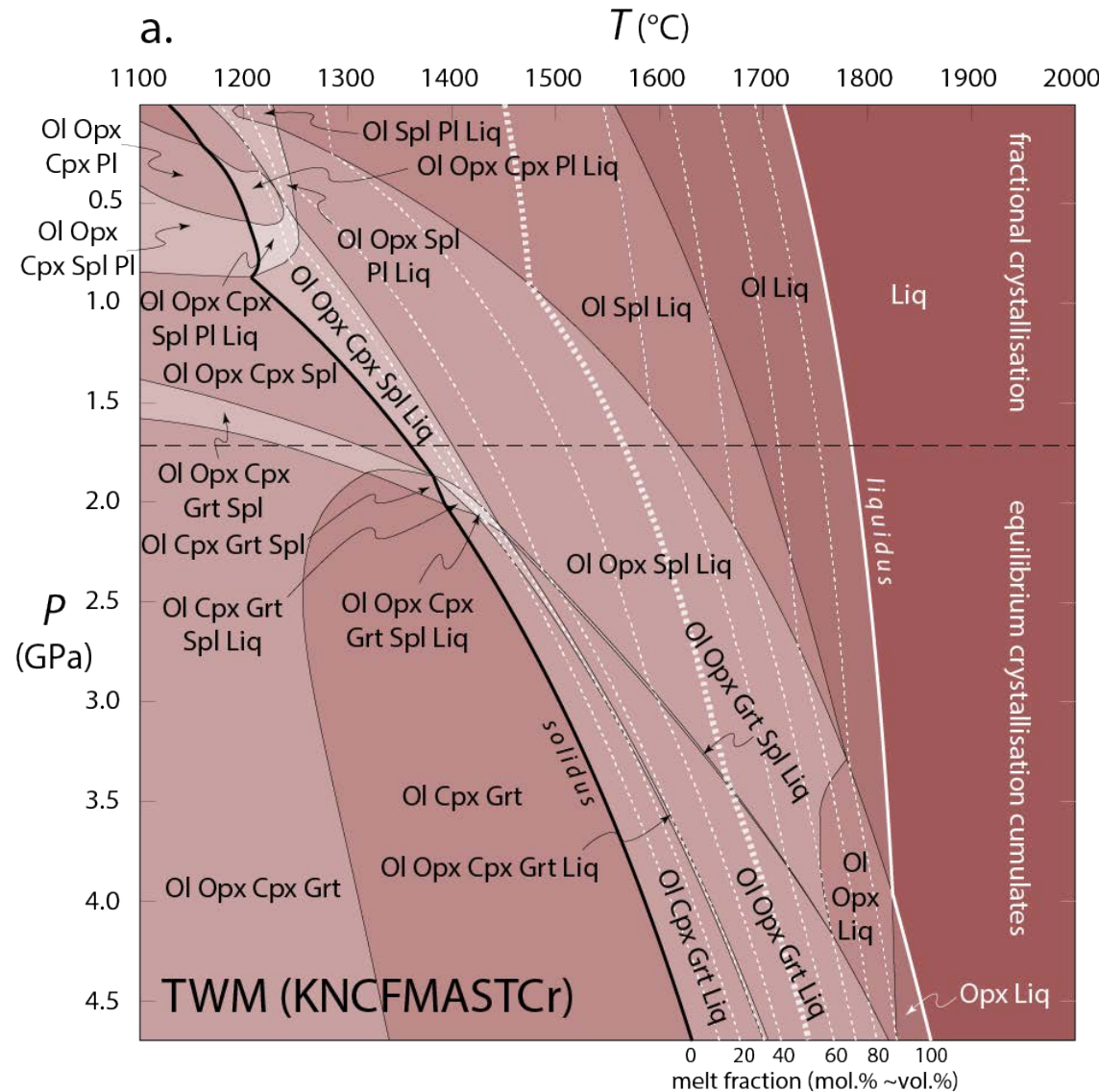
- A new paper provides a SINGLE melt model for calculating phase relations with respect to partial melting of lithologies ranging from peridotite to granite
- It includes a model for low-density silicate-bearing fluids, so works to much higher P
- If it is shown to work well, it is difficult to underestimate the importance of this development to phase equilibrium modelling...

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881

Melting whatever we like



- Extends the Jennings & Holland model into the **KNCFMASr** system

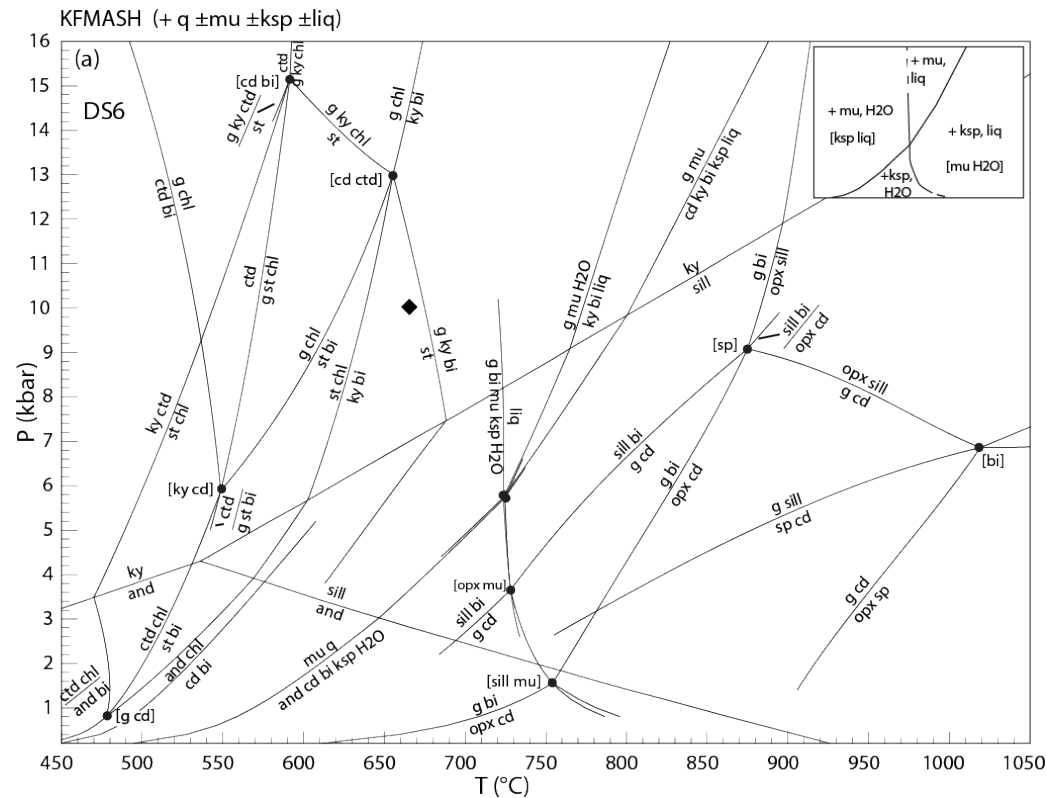
- Using these models, we can make whatever we like!

From Johnson et al. (in prep.)

Types of phase diagram:

P – T , T – X , P – X , 'modebox', etc.

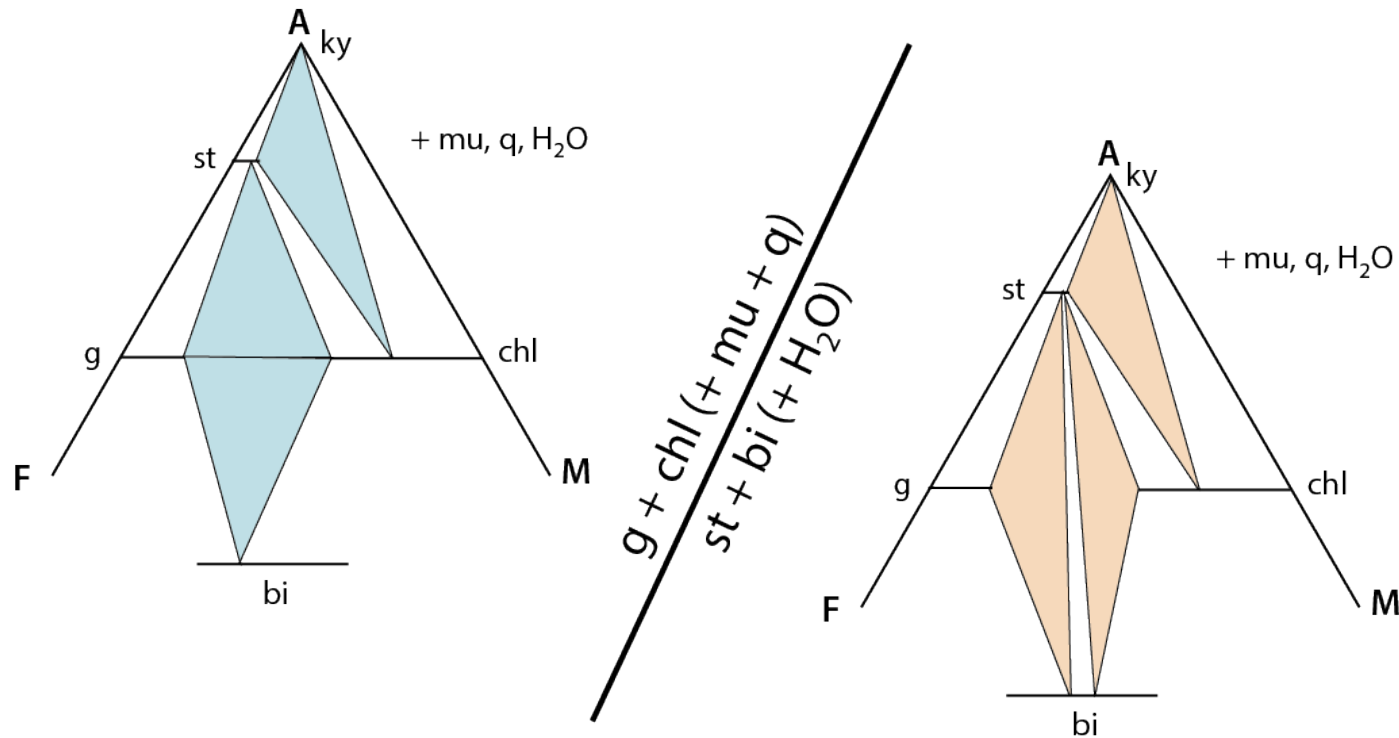
Types of diagram – P - T projections



From White et al. (2014a)

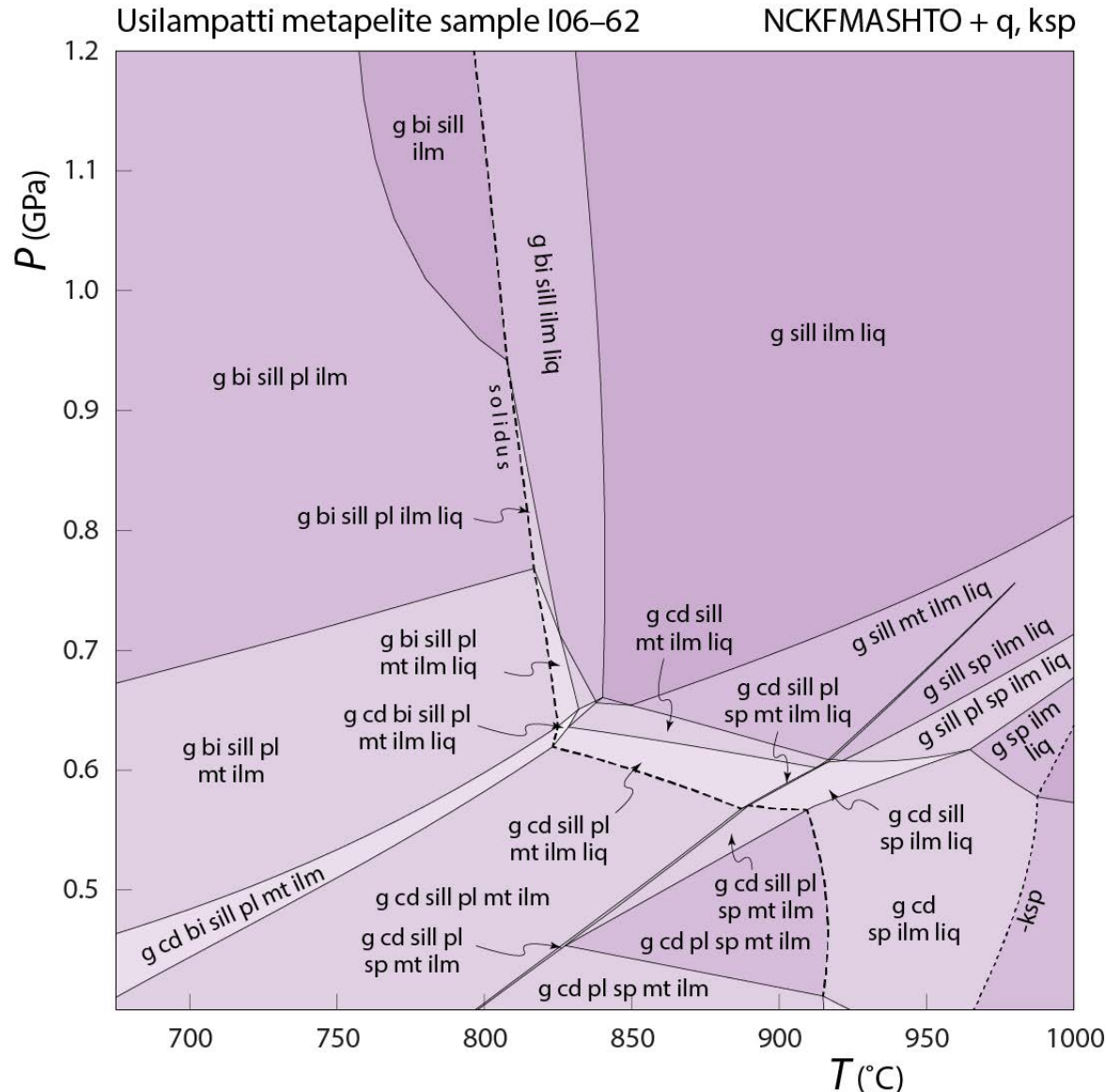
- AKA Schreinemaker's bundles, or petrogenetic grids
- All stable invariant points ($F = 0$) and univariant reactions ($F = 1$) projected onto the P - T plane
- Generally restricted to small systems (e.g. KFMASH) – informative but of little quantitative use in more realistic (= large) systems

Types of diagram – Compatibility diagrams



- Generally only of use in (artificially) small systems, such as KFMASH
- Very useful for thinking about what higher variance assemblages can be stable either side of a univariant reaction

Types of diagram – P–T pseudosections

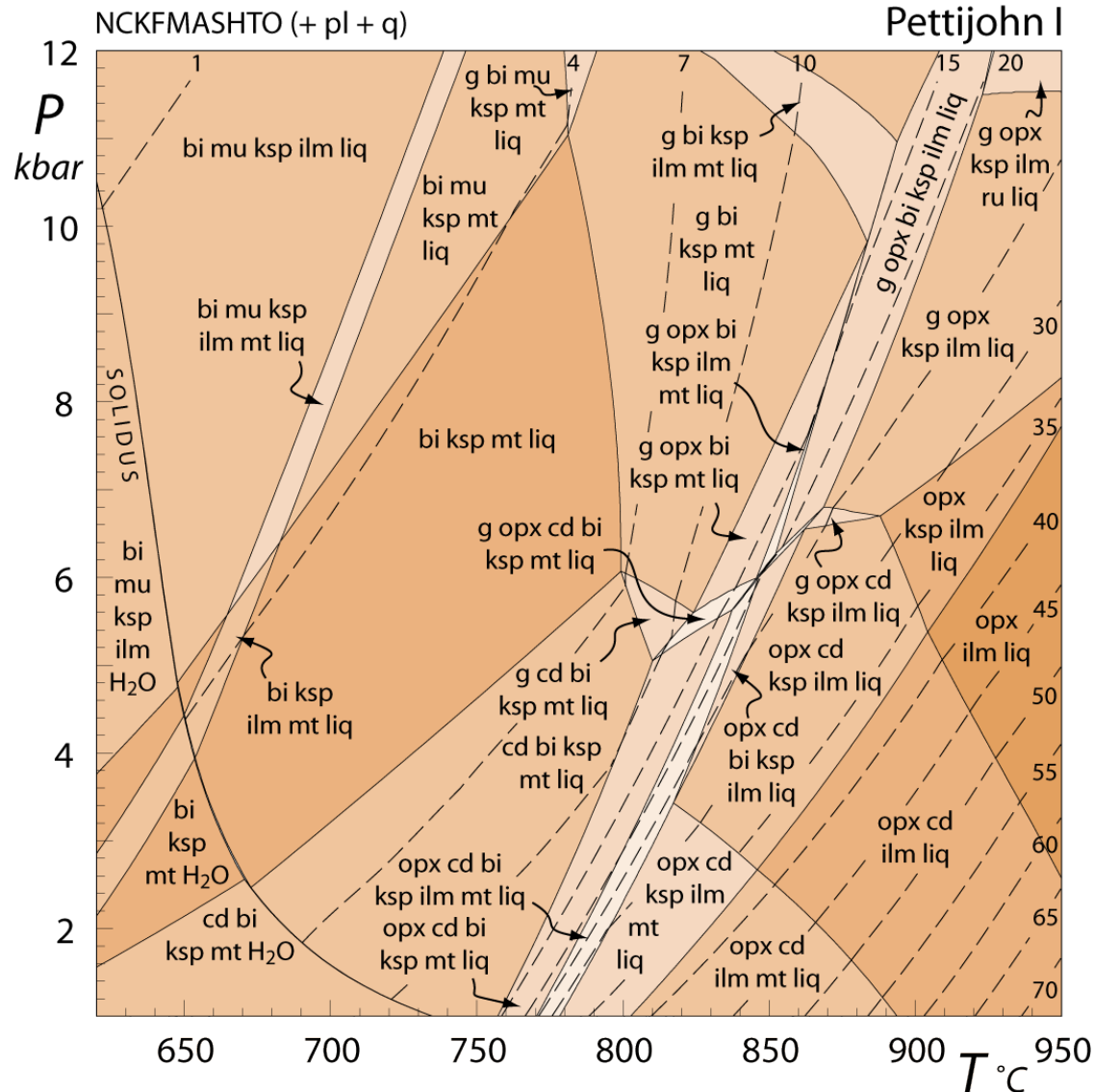


From Johnson et al. (2015)

- Most commonly drawn diagram
- Drawn for a **fixed bulk composition** (in this case in the NCKFMASHTO system)
- Simply a P – T map of the stable assemblages (paler = lower variance = more minerals, darker = higher variance = fewer minerals)

Tim Johnson, THERMOCALC short course, 2021

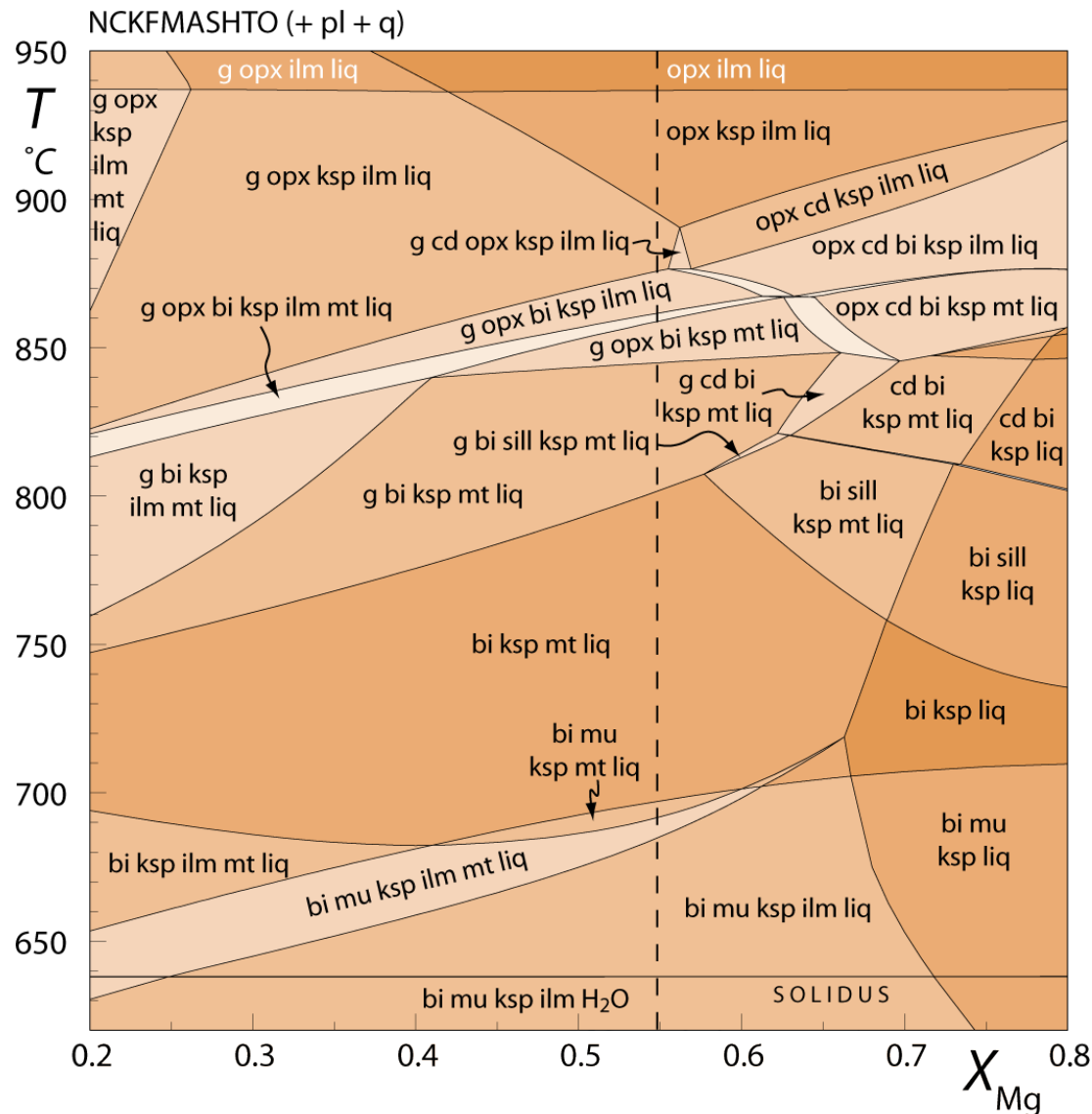
Contouring pseudosections



From Johnson *et al.* (2008)

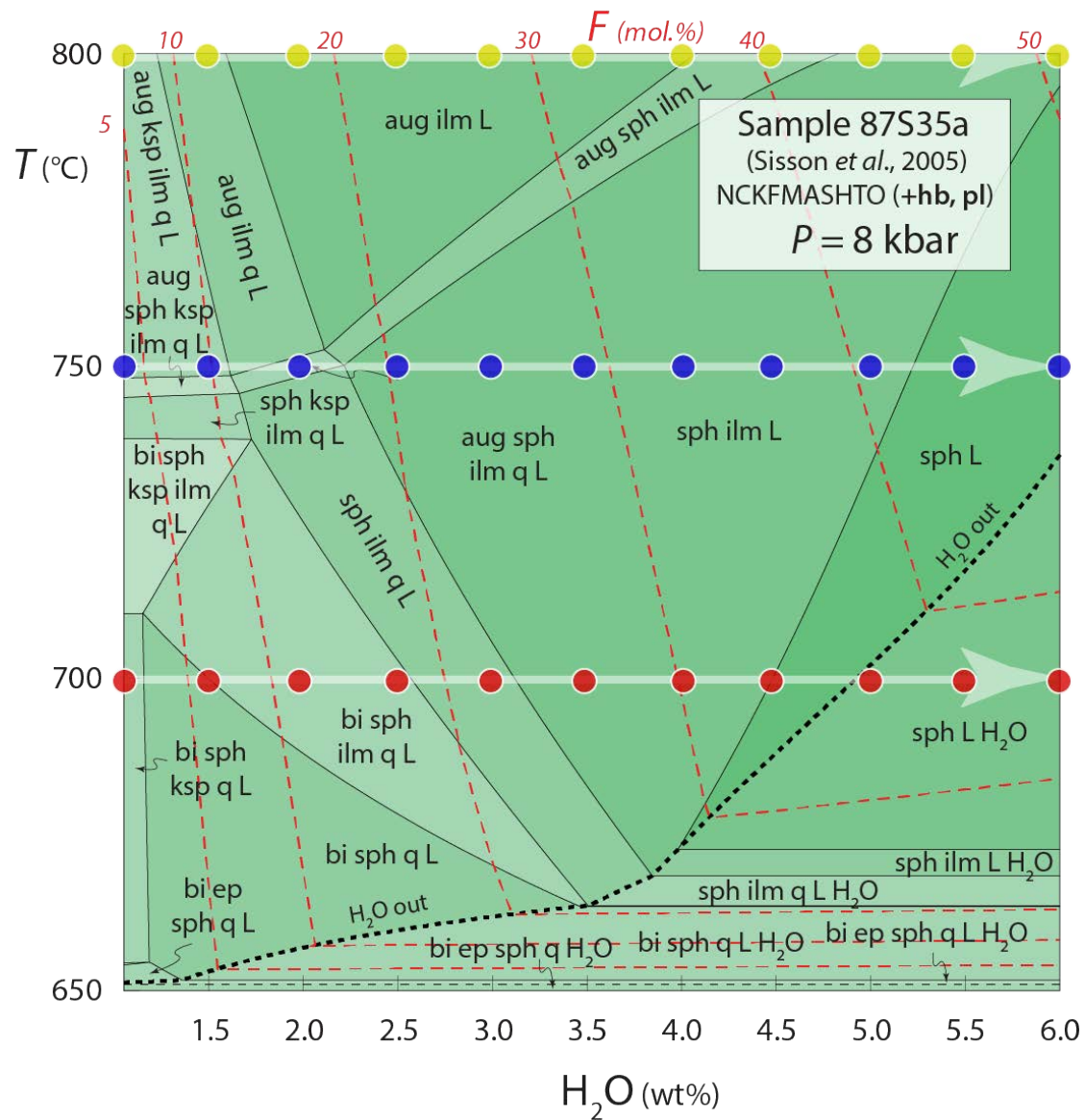
- Pseudosections are more useful when contoured for abundance and/or composition of phases
- Formally, all contouring was done 'by hand', line by line and point by point
- For THERMOCALC users, TCIInvestigator (Pearce *et al.* (2015) has made things MUCH easier...

P-X & T-X diagrams



- Requires either P (isobaric) or T (isothermal) to be fixed
- Allows examination of other variables, generally composition
- Of particular use are diagrams examining the effects of H_2O influx and melt loss

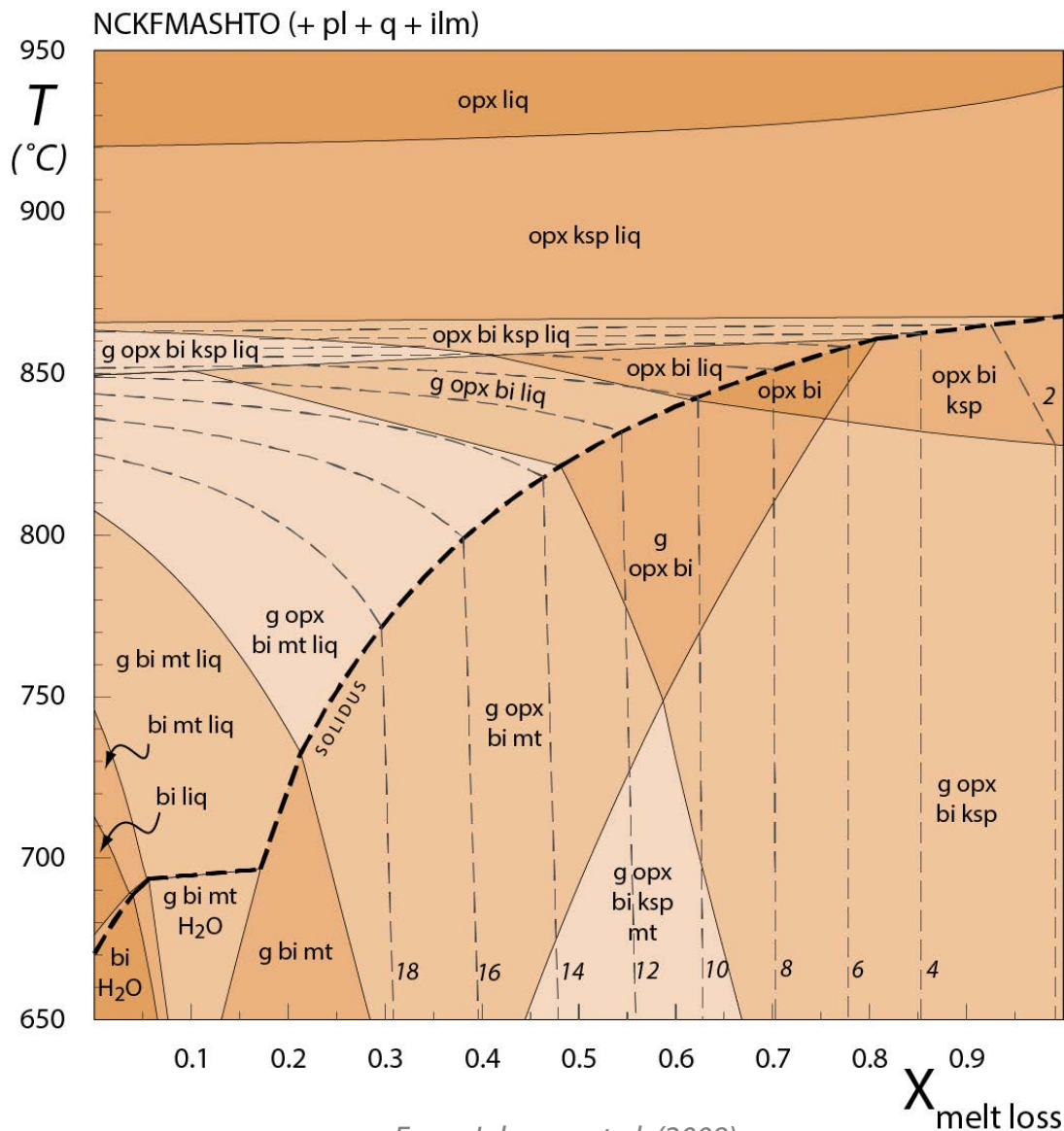
T - H_2O influx



- Melt fraction increases dramatically with H_2O influx
- May be a good analogy for melting at the base of arcs

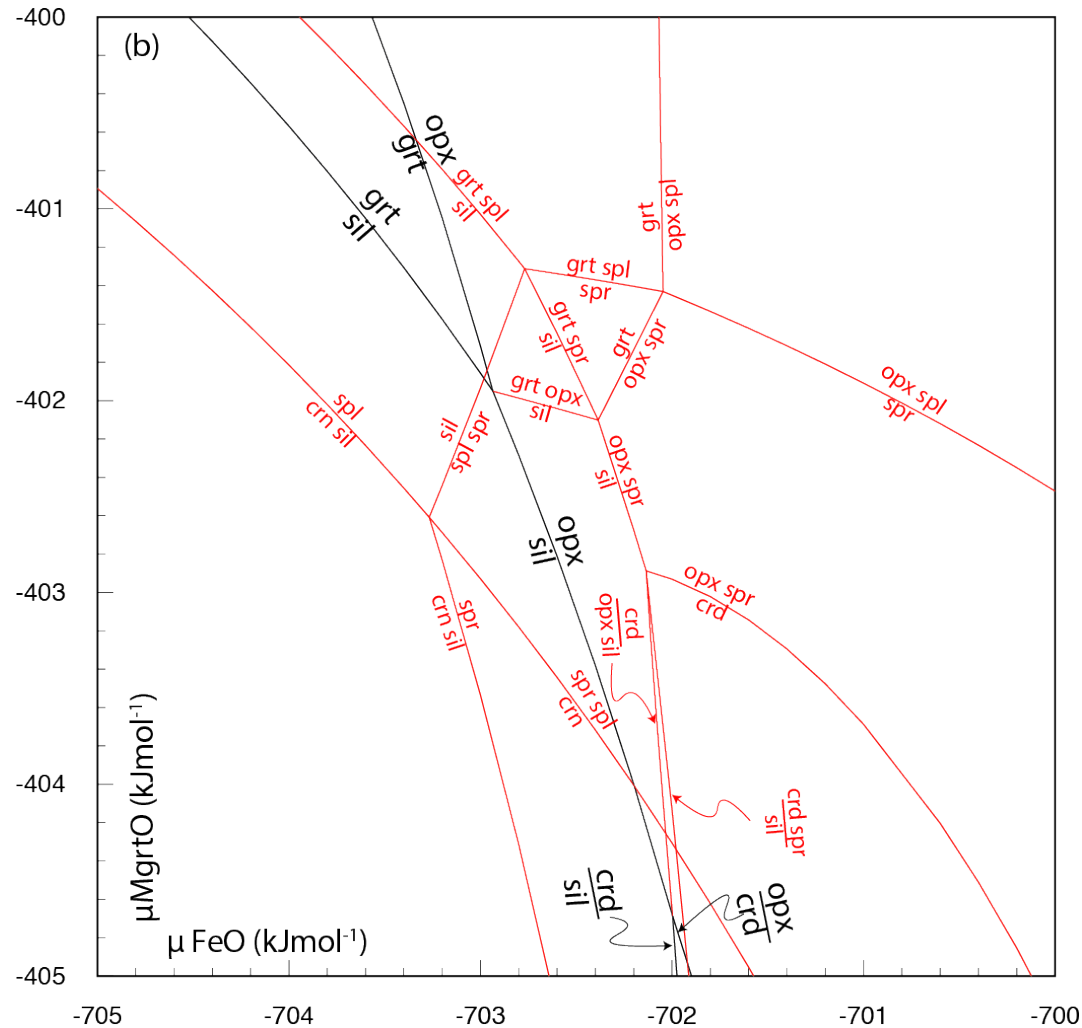
From Huang *et al.* in review

T-X melt loss



- Solidus migrates to higher T as melt is lost
- This is what permits preservation of 'dry' granulite facies assemblages

Chemical potential (μ - μ) diagrams

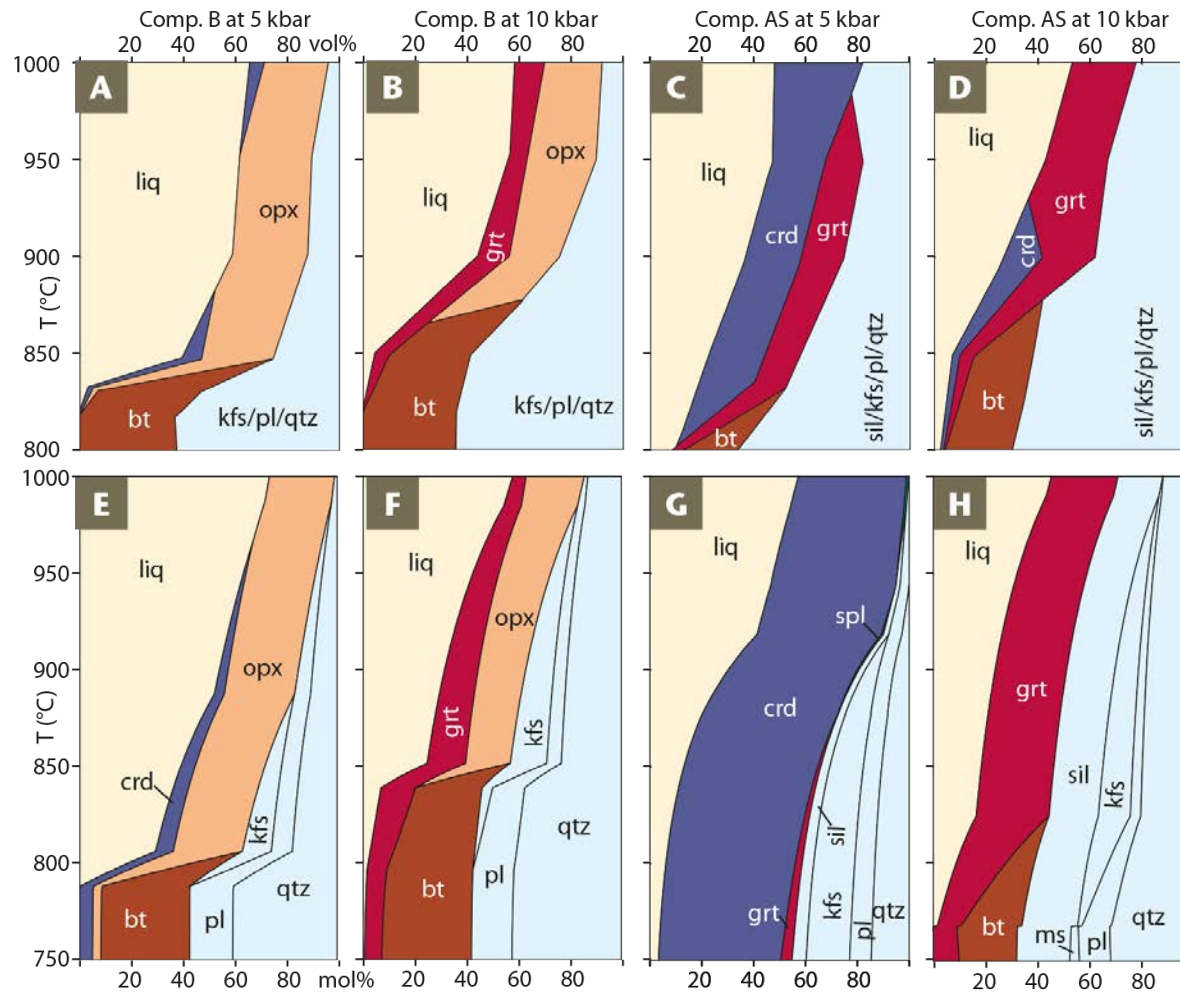


- Investigating transient disequilibrium and diffusion
- Permits examination of the spatial organization of microstructures

From Mitchell et al. (2019)

Tim Johnson, THERMOCALC short course, 2021

'Mode' v T (or P)



From White et al. (2011)

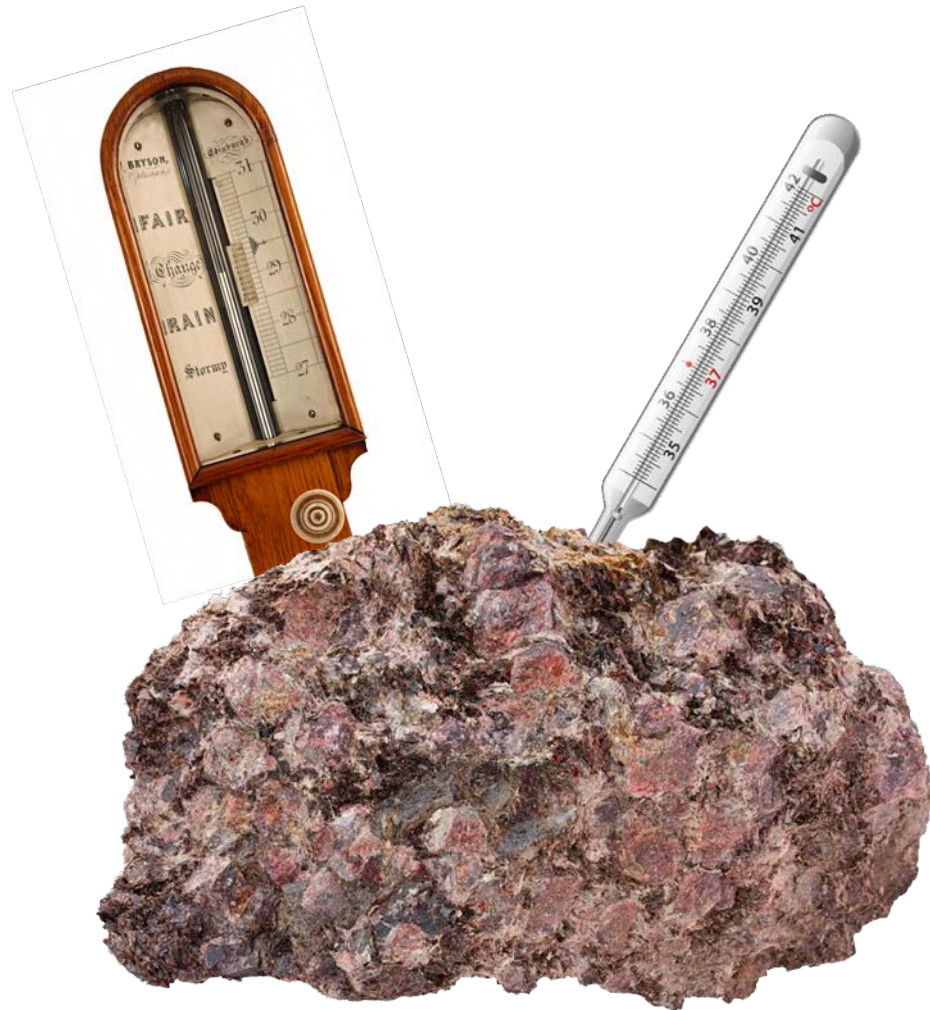
The match with experiments is decent – there are advantages and pitfalls with both methods

*An introduction to **THERMOCALC***

The nuts and bolts of calculations



So, you've identified a rock you'd like to model...



What is required?

- The bulk rock composition in terms of major element oxides:
- XRF or dissolution ICP–MS (+/- Fe-titration);
- point-counting or X-ray maps and mineral chemistry;
- existing (literature) data.



It's very cheap!

The importance of sampling properly

- Usually choose samples with the lowest variance = most minerals
- Select samples that are as HOMOGENEOUS as possible
- If the sample is heterogeneous, separate homogeneous portions (by saw) prior to crushing/powdering



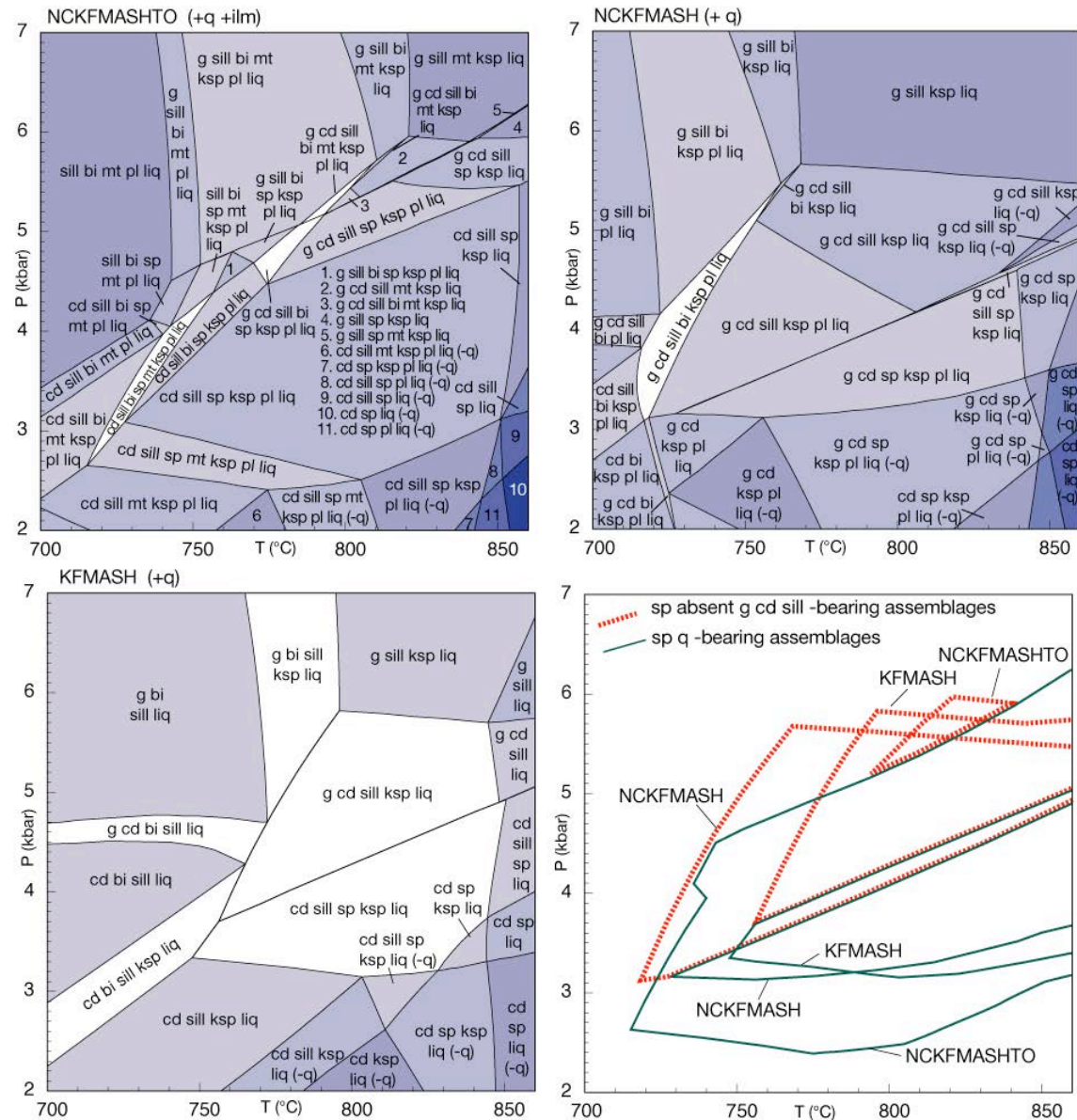
It's very cheap!

Bulk compositions – weight% to mol.%

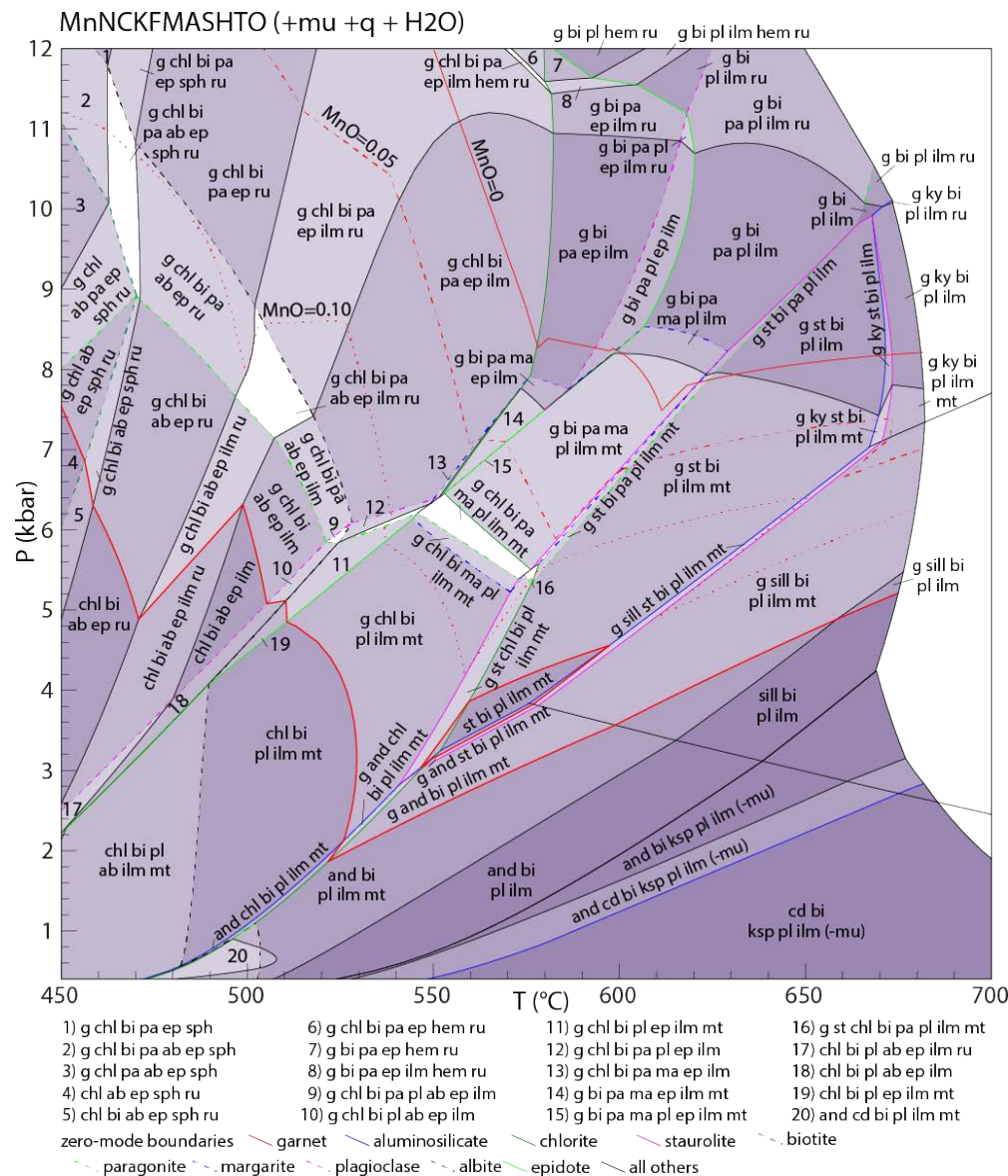
- THERMOCALC requires that you input the bulk composition in MOLES of the components (oxides) = MO; XRF analyses come as WEIGHT% oxides = WO
- To convert to MO, you need to divide WO by the molecular weight (MW) of the oxides (**MO = WO/MW**), then normalize to 100% (although THERMOCALC will automatically normalize for you)
- You need to make decisions about ferric iron and H₂O, and think about those components that are cannot (currently) be modelled, such as P₂O₅. We'll get to this later...
- See the file '**bulk compositions.xls**' ...



The choice of chemical system

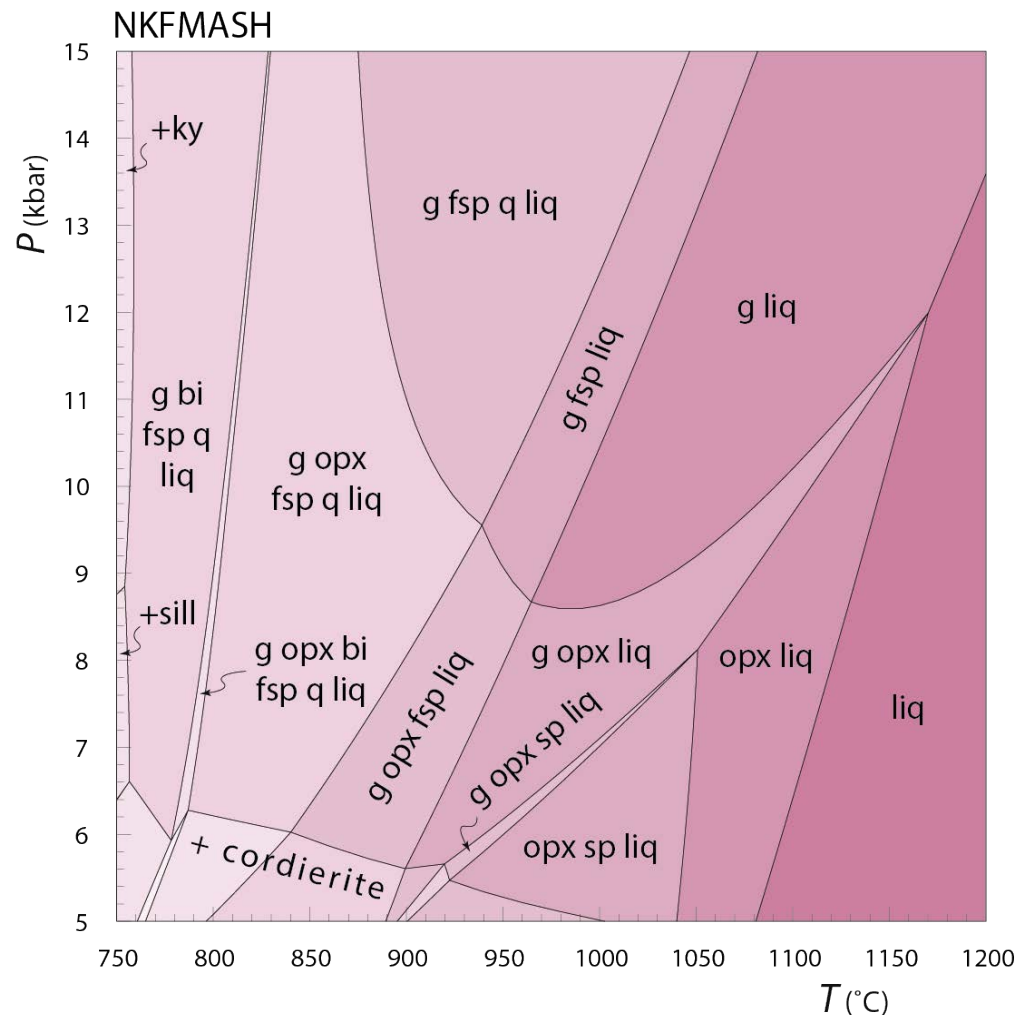


The choice of chemical system



- Largest available system is MnNCKFMASHTO (for 'pelites & mafic) or NCKFMASHTOCr (mafic & ultramafic)
- TiO₂ (T) and Fe₂O₃ (O) allow more realistic treatment of silicates and consideration of Fe–Ti oxides (rutile, ilmenite, magnetite, hematite)
- Mn mainly affects garnet stability
- A limitation is that the contents of H₂O and ferric/ferrous iron are educated guesswork...
- Another is that there are many other (minor/trace) elements that cannot currently be modelled...

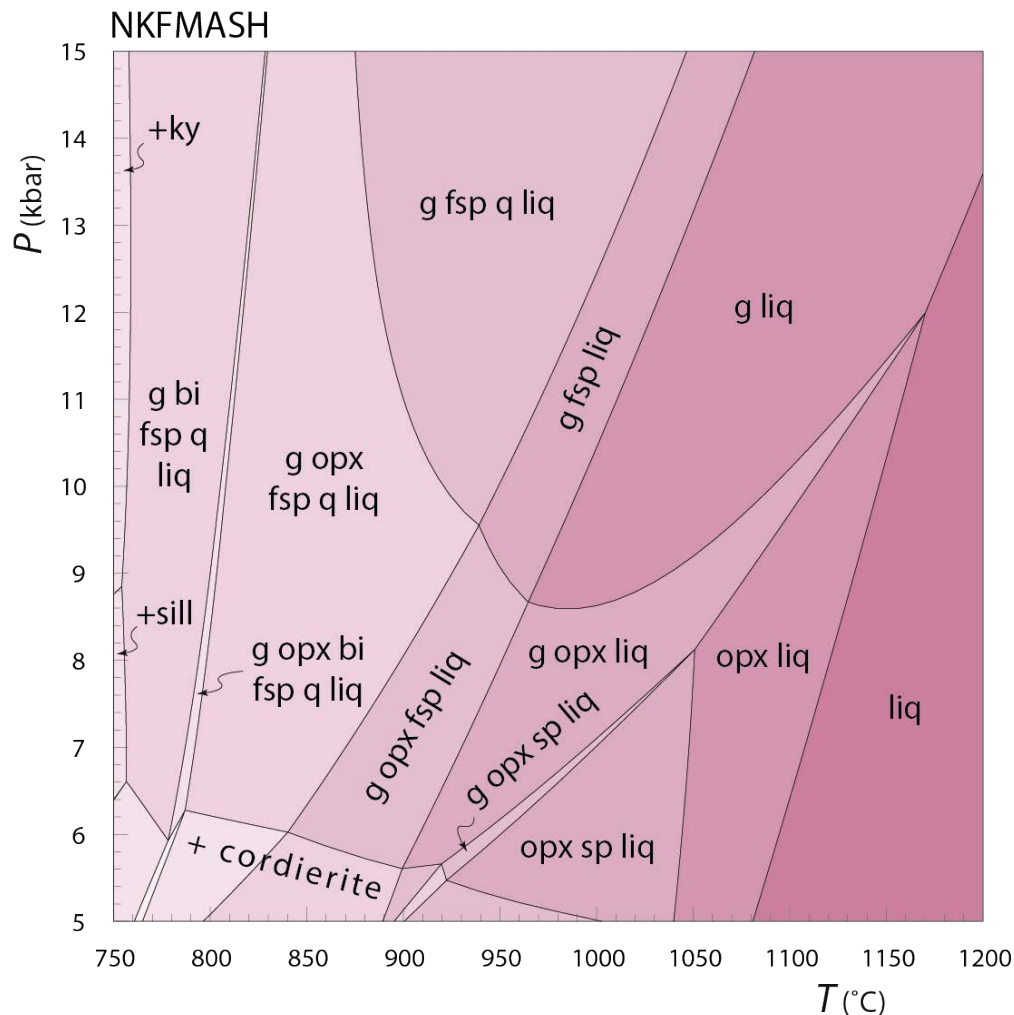
Pseudosections – logic puzzles



- P – T pseudosections are drawn for a single bulk composition (a 'rock')
- They consist of fields that represent mineral assemblages
- Darker shade = **HIGHER** variance = **FEWER** minerals ($F = C - P + 2$)
- We try to match the calculated stability of mineral assemblages with the assemblages we observe in our rocks

P–T pseudosection based on the bulk composition of the experimental starting materials of Rich Taylor (e.g. Taylor et al., 2015)

Pseudosections – logic puzzles



P-T pseudosection based on the bulk composition of the experimental starting materials of Rich Taylor (e.g. Taylor et al., 2015)

- The assemblage fields are bounded by lines and points
- Each and every point* has **FOUR** lines emanating from it
- Crossing a line represents to appearance or disappearance of a phase (F changes by 1)
- In other words, a line represents where the abundance ('mode') of a mineral goes to zero
- A point is where the modes of two minerals go to zero

*** Except UNIVARIANT LINES!**

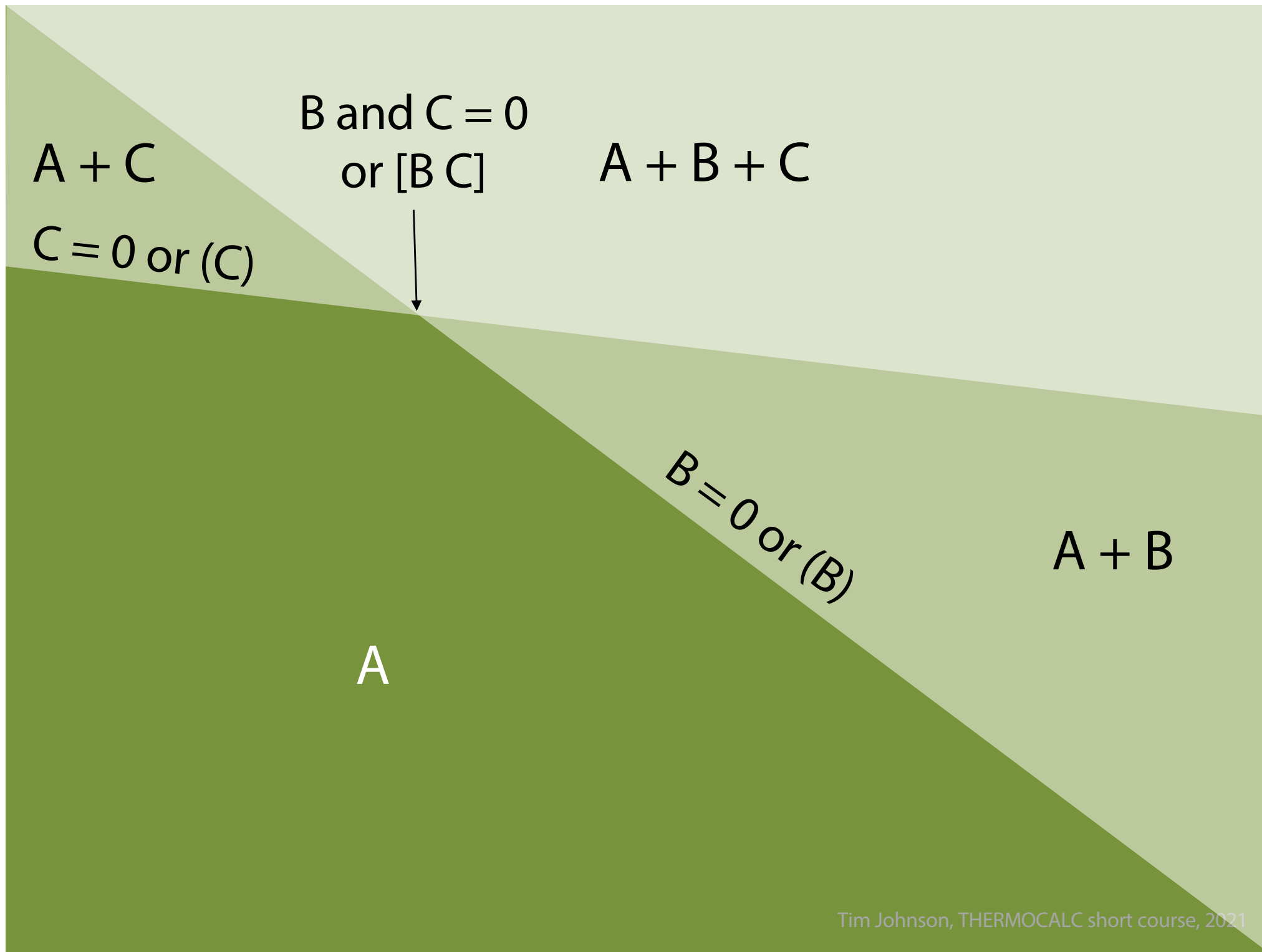
A

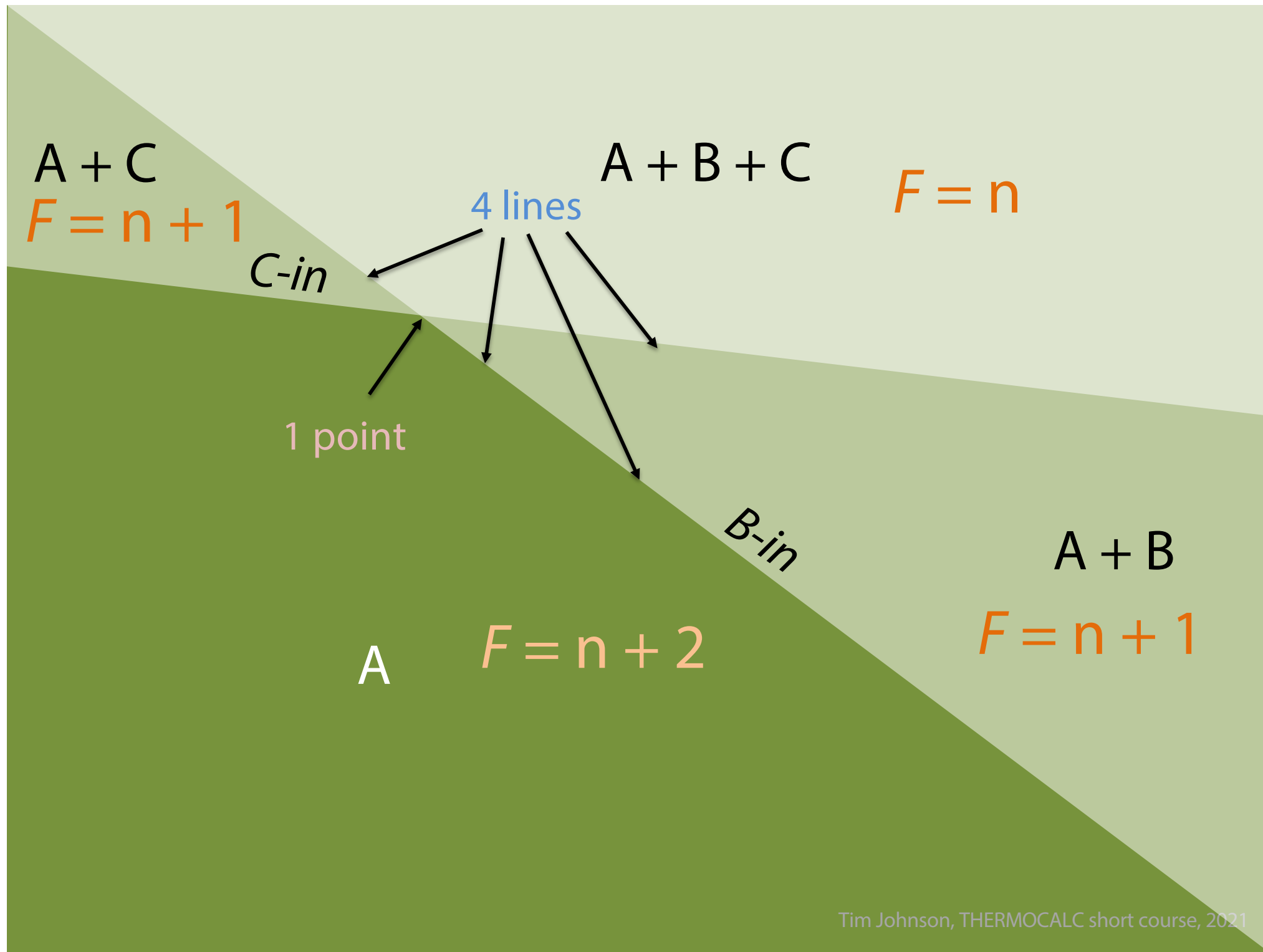


A

$B = 0$ or (B)

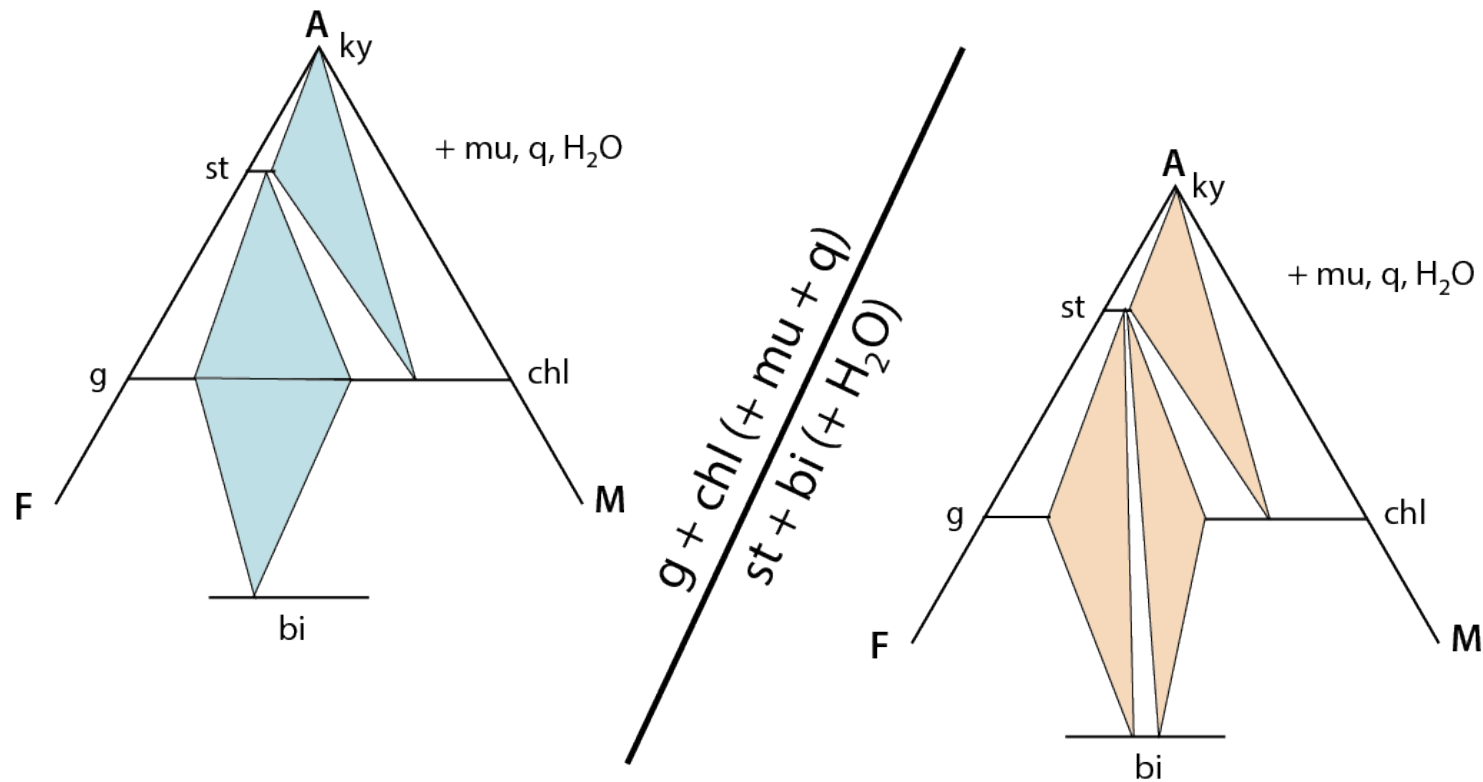
A + B





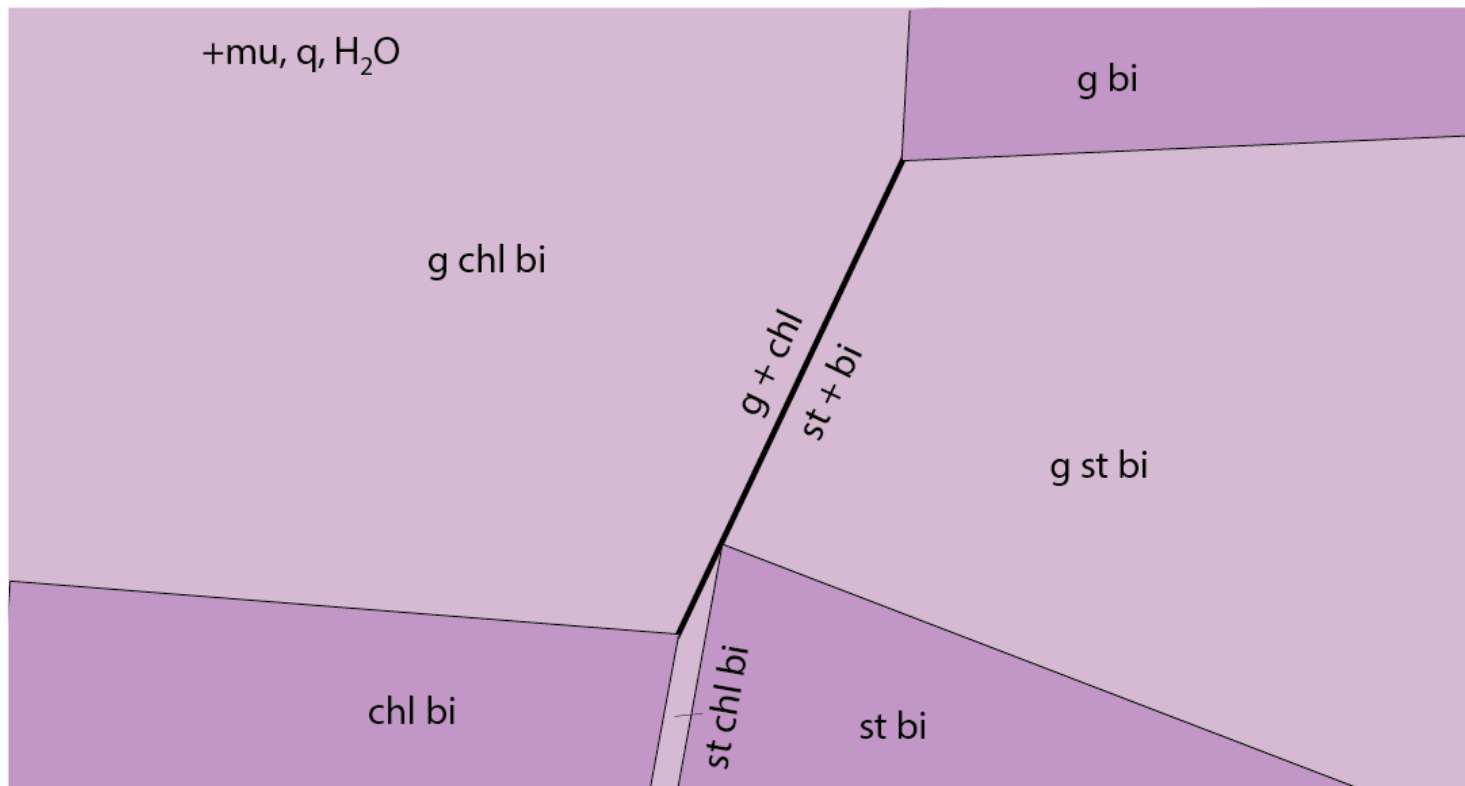
Pseudosections – logic puzzles

- **UNIVARIANT LINES** (discontinuous reactions) behave exactly the same providing you think about them as INFINITELY THIN FIELDS...



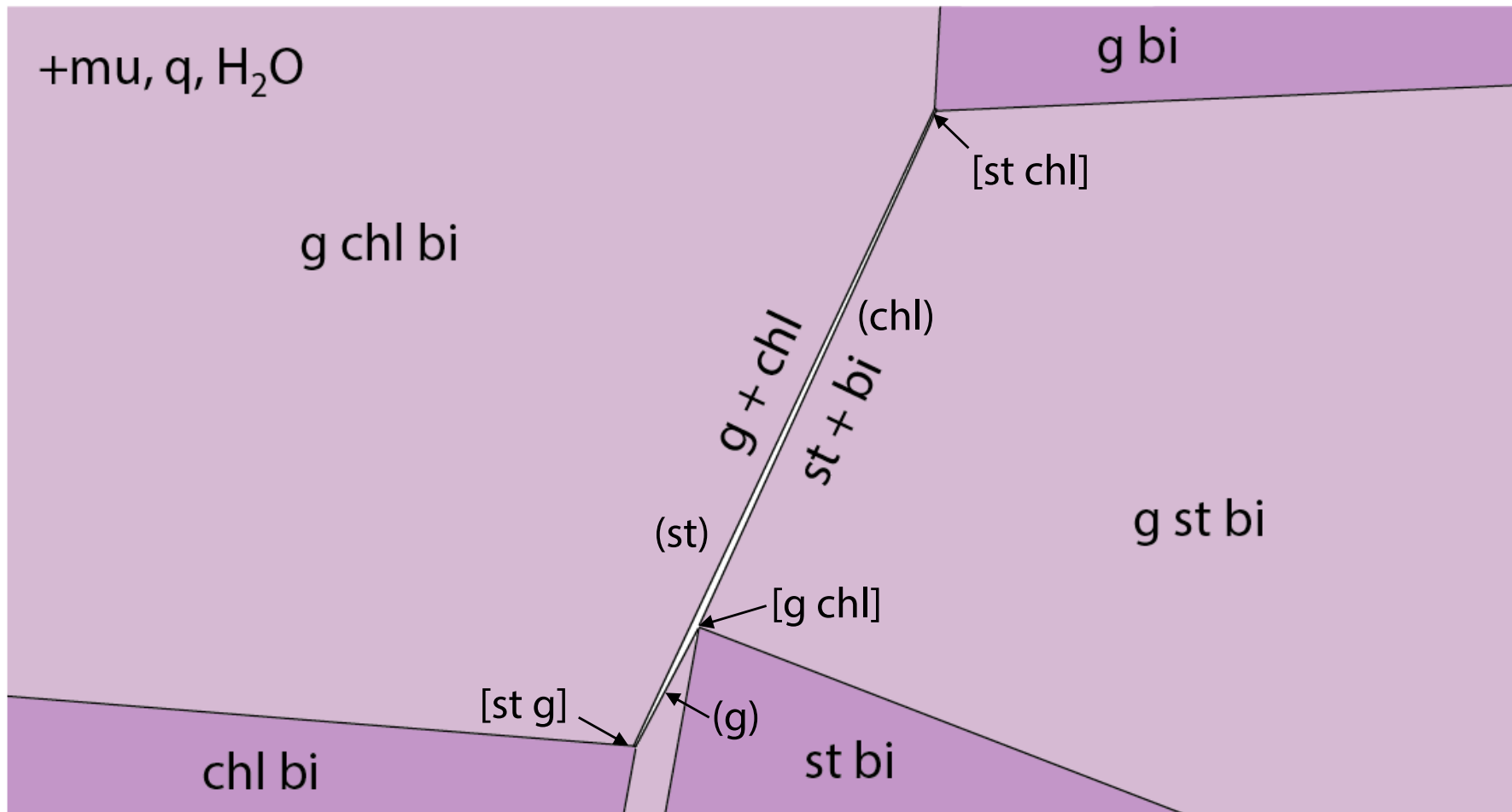
Pseudosections – logic puzzles

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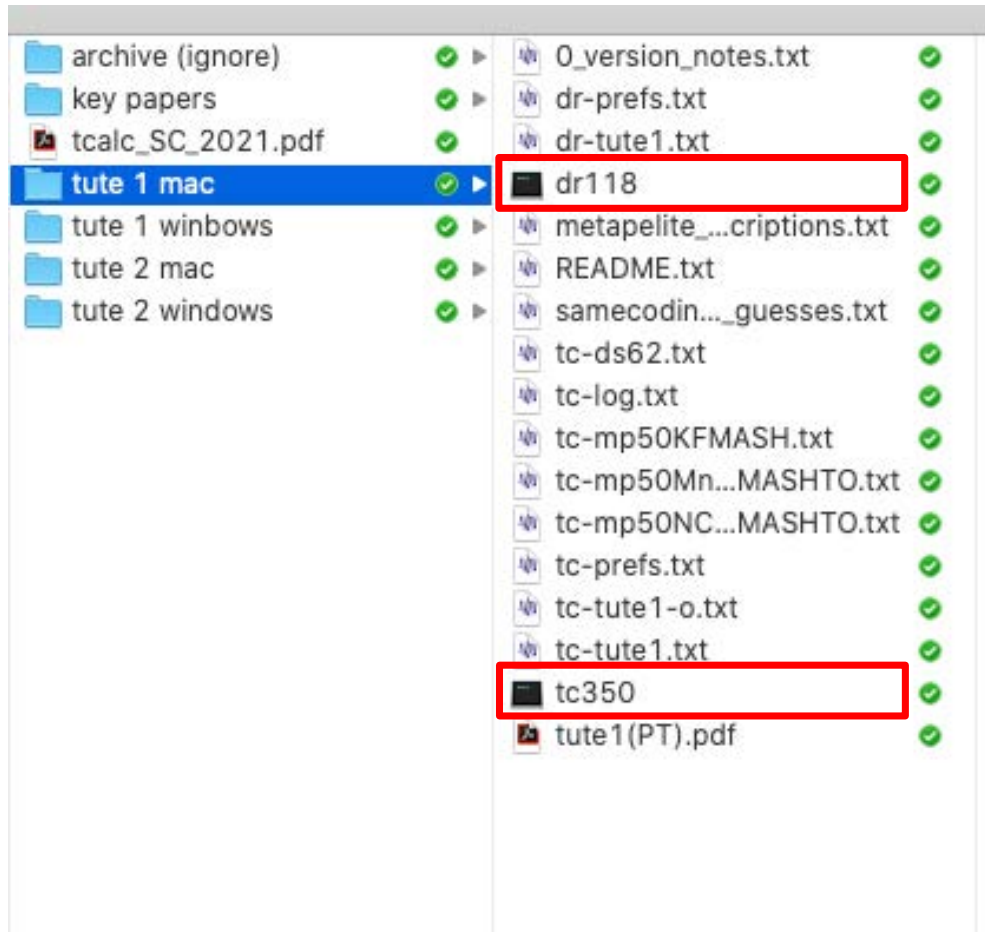


Pseudosections – logic puzzles

- **UNIVARIANT LINES** (discontinuous reactions) behave exactly the same providing you think about them as infinitely thin fields...

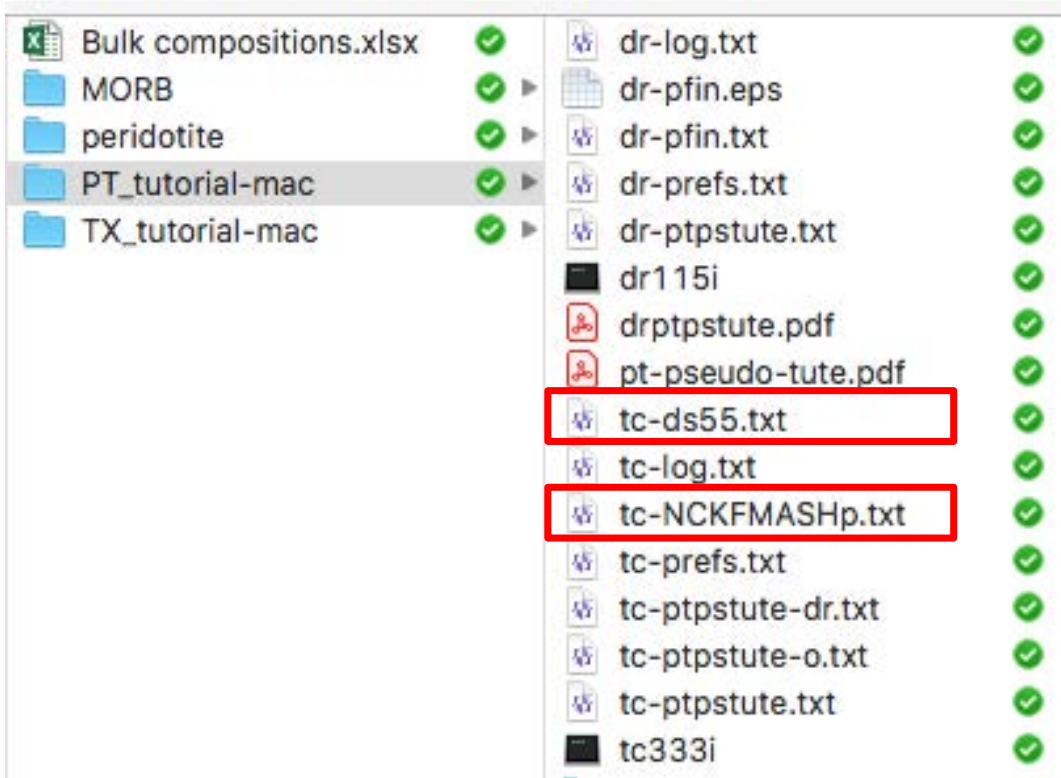


THERMOCALC files



- There are two programs, **THERMOCALC** (in this case tc333i) and **drawpd** (in this case dr115i)
- **THERMOCALC** is for running the calculations (there are many different versions)
- **drawpd** is for plotting the diagrams (there are many different versions)

THERMOCALC files



- There are two data files, **tc-ds55.txt** and **tc-NCKFMASHp.txt**
- **tc-ds55.txt** is the Holland & Powell end-member thermodynamic data (in this case the 1998 version)
- **tc-NCKFMASHp.txt** contains the activity–composition models for the different minerals
- THESE FILES ARE **LOOK BUT DO NOT TOUCH**

THERMOCALC files

$$0 = \Delta G + RT \ln K$$

end-member data

solution models

Journal of
METAMORPHIC GEOLOGY

J. metamorphic Geol., 2011, **29**, 333–383 doi:10.1111/j.1525-1314.2010.00923.x

An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids

T. J. B. HOLLAND¹ AND R. POWELL²

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ABSTRACT The thermodynamic properties of 254 end-members, including 210 mineral end-members, 18 silicate liquid end-members and 26 aqueous fluid species are presented in a revised and updated internally consistent thermodynamic data set. The *PVT* properties of the data set phases are now based on a modified Tait equation of state (EOS) for the solids and the Pitzer & Sterner (1995) equation for gaseous components. Thermal expansion and compressibility are linked within the modified Tait EOS (TEOS) by a thermal pressure formulation using an Einstein temperature to model the temperature dependence of both the thermal expansion and bulk modulus in a consistent way. The new EOS has led to improved fitting of the phase equilibrium experiments. Many new end-members have been added, including several deep mantle phases and, for the first time, sulphur-bearing minerals. Silicate liquid end-members are in good agreement with both phase equilibrium experiments and measured heat of melting. The new dataset considerably enhances the capabilities for thermodynamic calculation on rocks, melts and aqueous fluids under crustal to deep mantle conditions. Implementations are already available in THERMOCALC to take advantage of the new data set and its methodologies, as illustrated by example calculations on sapphirine-bearing equilibria, sulphur-bearing equilibria and calculations to 300 kbar and 2000 °C to extend to lower mantle conditions.

Key words: equation of state; internally consistent dataset; thermodynamic data.

Holland & Powell (2011)

Journal of
METAMORPHIC GEOLOGY

J. metamorphic Geol., 2014, **32**, 261–286 doi:10.1111/jmg.12071

New mineral activity–composition relations for thermodynamic calculations in metapelitic systems

R. W. WHITE,¹ R. POWELL,² T. J. B. HOLLAND,³ T. E. JOHNSON^{1,*} AND E. C. R. GREEN¹

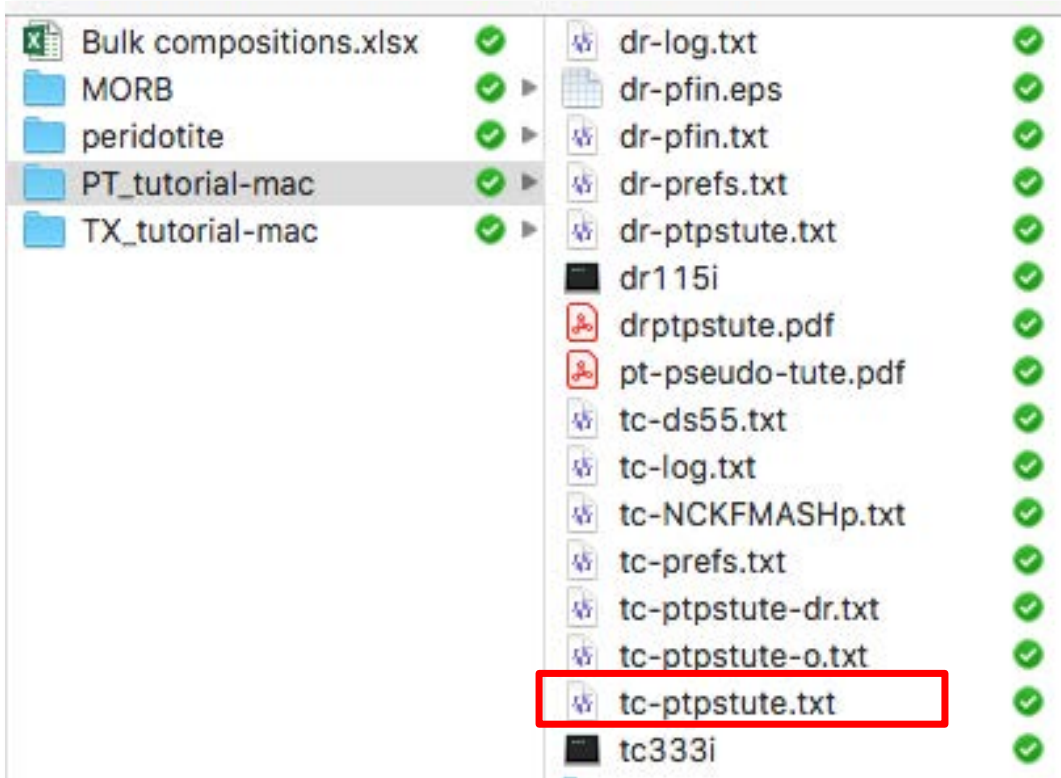
¹Institute of Geoscience, University of Mainz, D-55099, Mainz, Germany
²School of Earth Sciences, University of Melbourne, Melbourne, Vic.3010, Australia
³Department of Earth Sciences, University of Cambridge, Cambridge, CB2 3EQ, UK
*Present address: Department of Applied Geology, The Institute for Geoscience Research (TiGeR), Curtin University, GPO Box U1987, Perth, WA 6845, Australia

ABSTRACT New activity–composition (*a*–*x*) relations for minerals commonly occurring in metapelites are presented for use with the internally consistent thermodynamic dataset of Holland & Powell (2011, *Journal of Metamorphic Geology*, **29**, 333–383). The *a*–*x* relations include a broader consideration of Fe₂O₃ in minerals, changes to the formalism of several phases and order-disorder in all ferromagnesian minerals where Fe–Mg mixing occurs on multiple sites. The *a*–*x* relations for chlorite, biotite, garnet, chloritoid, staurolite, cordierite, orthopyroxene, muscovite, paragonite and margarite have been substantially reparameterized using the approach outlined in the companion paper in this issue. For the first time, the entire set of *a*–*x* relations for the common ferromagnesian minerals in metapelitic rocks is parameterized simultaneously, with attention paid to ensuring that they can be used together to calculate phase diagrams of geologically appropriate topology. The *a*–*x* relations developed are for use in the Na₂O–CaO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O–TiO₂–O₂ (NCKFMASHTO) system for both subsolidus and suprasolidus conditions. Petrogenetic grids in KFMASH and KFMASHTO are similar in topology to those produced with earlier end-member datasets and *a*–*x* relations, but with some notable differences. In particular, in subsolidus equilibria, the FeO/(FeO + MgO) of garnet is now greater than in coexisting staurolite, bringing a number of key staurolite-bearing equilibria into better agreement with inferences from field and petrographic observations. Furthermore, the addition of Fe³⁺ and Ti to a number of silicate phases allows more plausible equilibria to be calculated in relevant systems. Pseudosections calculated with the new *a*–*x* relations are also topologically similar to equivalent diagrams using earlier *a*–*x* relations, although with many low variance fields shifting in *P*–*T* space to somewhat lower pressure conditions.

Key words: *a*–*x* relations; metapelite; NCKFMASHTO; pseudosection; THERMOCALC.

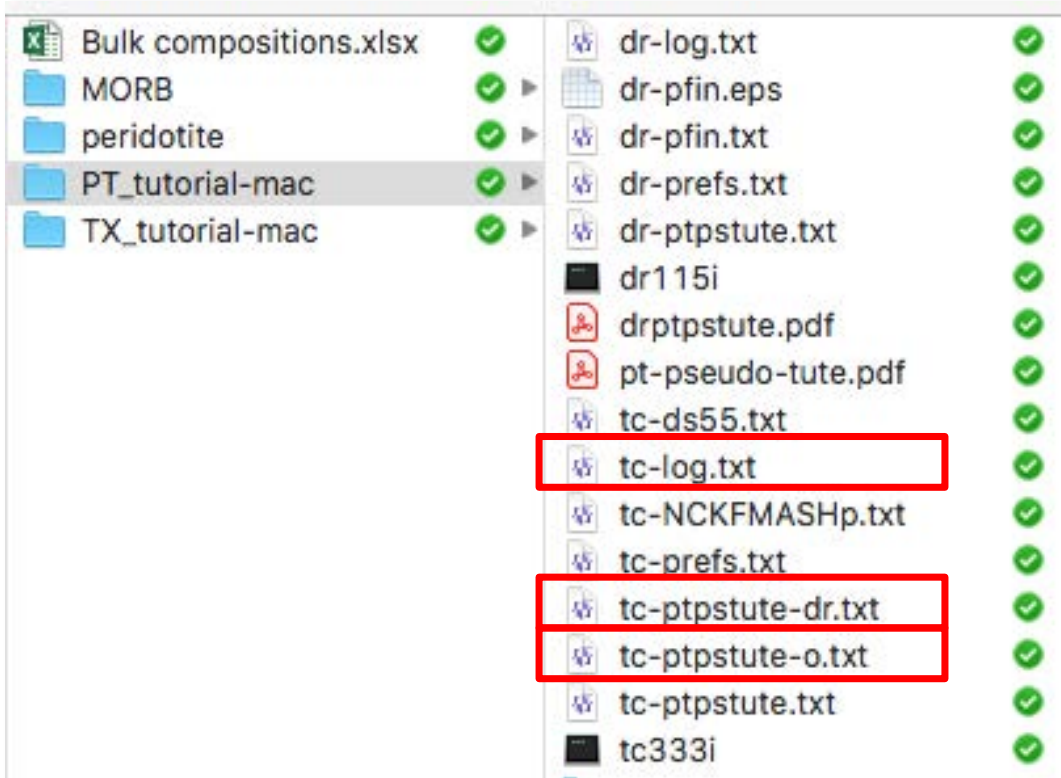
White et al. (2014a)

THERMOCALC files



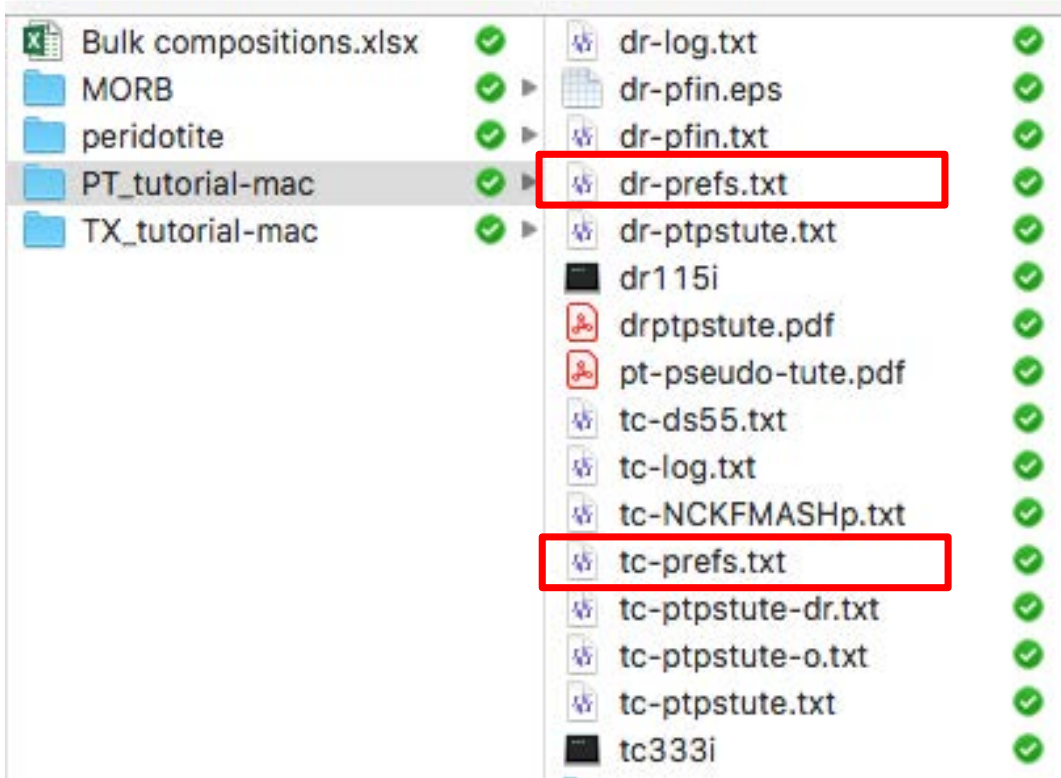
- The file containing user specific input, here called **tc-ptpstute.txt**, is called the script file
- Here you input your bulk composition, the P – T window of interest, and many other scripts allowing control of many aspects of THERMOCALC , (both input and output)

THERMOCALC files



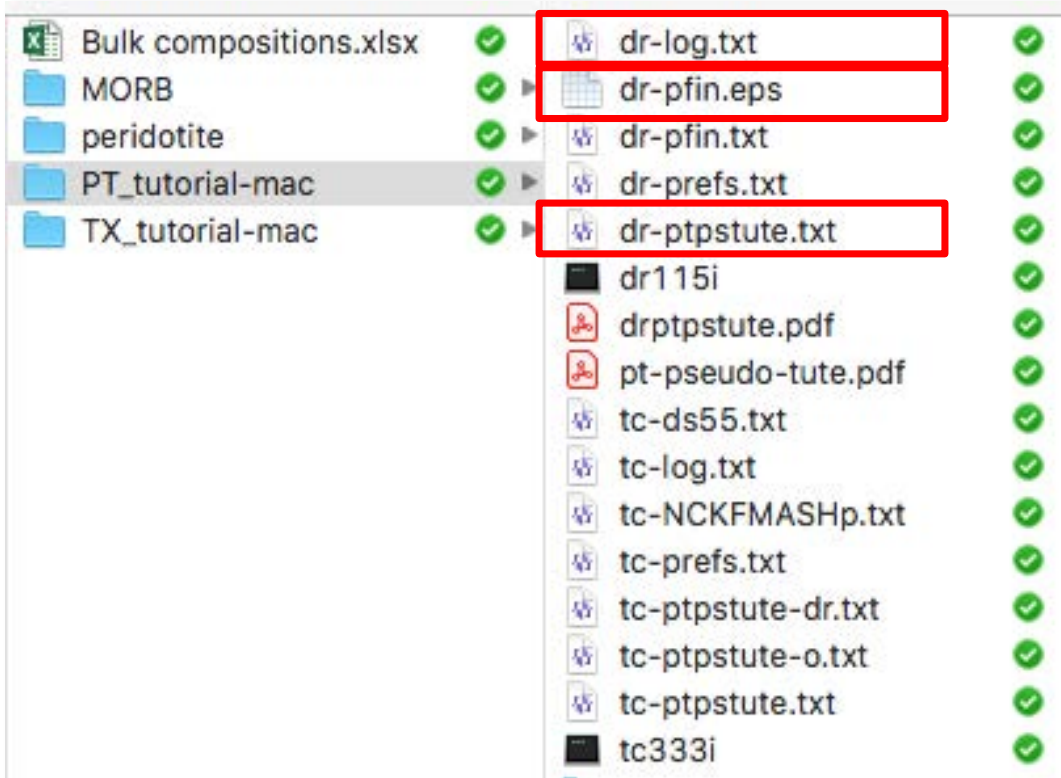
- Three files (in this version of tcalc) are automatically generated when you run THERMOCALC
- The output file (**tc-ptpstute-o.txt**) contains, well, output...
- The drawpd file (**tc-ptpstute-dr.txt**) contains the coordinates of lines and points to paste into a drawpd script file (**dr-ptpstute.txt**)
- The log file (**tc-log.txt**) contains detailed output, including starting compositions, bulk compositions, etc...

THERMOCALC files



- Two files (**tc-prefs.txt** and **dr-prefs.txt**) allow users to specify some first-order preferences
- For example, in **tc-prefs.txt** you can specify the type of calculation, the end-member thermodynamic data to be used, and the width of the console window
- In both prefs files, you can tell THERMOCALC and drawpd which script file to work with, which saves lots of time

THERMOCALC files



- The files (**dr-ptpstute.txt** contains everything that drawpd needs to draw the phase diagram
- This includes the data for lines and points, which data to plot on which axes, what colour to use to shade fields, whether or not to number lines, etc.
- When you run this file through drawpd it (should) make a nice encapsulated postscript file (dr-ptpstute.eps)
- Details of the drawpd calcs can be found in **dr-log.txt**

THERMOCALC files

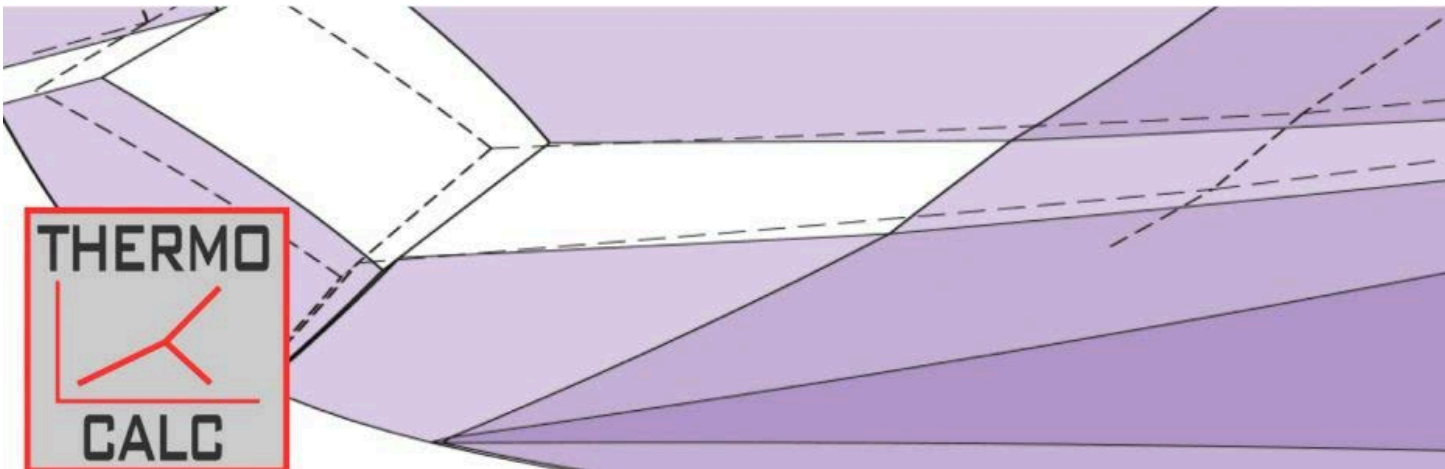
tidy
DESKTOP
tidy
MIND

- You will save yourself lots of time if you get into the habit of organizing your desktop so that you know where all of the windows and files are...



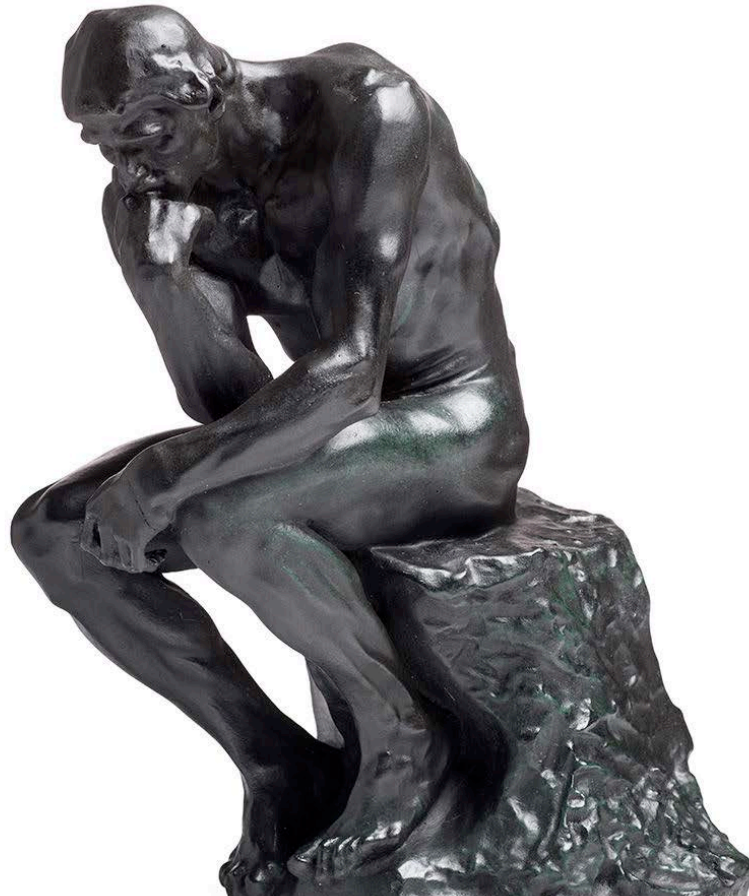
THERMOCALC

tips and tricks



Bulk compositions – problem components

- You can and will save yourself lots of time by thinking about what you want to do and how you want to do it BEFORE you start any calculations
- A thorough characterisation of your samples using field and petrographic observations is required prior to going anywhere near thermodynamic calculations



Bulk compositions – problem components

- The bulk composition you use can only ever be an approximation of the real composition. Many minor and almost all trace elements have to be ignored.
- P_2O_5 – in most rocks, P_2O_5 is mostly in apatite. However, this leaves an excess of Ca which must go somewhere, affecting the stability of other Ca-bearing phases
- To account for the presence of apatite, subtract an amount of Ca equal to $3.33 \times P_2O_5$ **ONCE YOU HAVE CONVERTED TO MOL.%**
- However, you might have lots of monazite...



Bulk compositions – problem components

- H_2O – some rocks (like mantle peridotite) are nominally 'dry' and you can ignore H_2O
- Most crustal metamorphic rocks contain hydrous minerals, so H_2O is rather important
- When modelling subsolidus conditions (the rocks haven't melted), for most compositions you can consider H_2O to be in excess (it is constantly being produced by dehydration reactions)
- In migmatites, the amount of H_2O governs the amount of melt, so you have to 'guess' an appropriate amount of H_2O



Bulk compositions – problem components

- If your rocks are unaltered, the loss on ignition (LOI) from an XRF analysis is a decent approximation
- However, not if you have lots of cordierite (CO_2) or other volatile-bearing minerals
- You can also estimate H_2O (and other components) using mineral chemistry and the calculated modes of H_2O -bearing minerals in thin sections
- You can commonly make an educated guess on an appropriate H_2O content, for example, enough to just saturate the solidus as a reasonable P



Bulk compositions – problem components

- Ferric iron (Fe^{3+}) – ferric iron is VERY important for the stability of many minerals, both major and accessory minerals
- You can measure (via titration) the amounts of FeO and Fe_2O_3 , which will only give you a MAXIMUM amount of Fe_2O_3 (rocks don't tend to become more reduced in the atmosphere)
- Unless you have shed-loads of magnetite or ilmenite, a good guess is to use an $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.1 for Archaean rocks, and 0.2 for younger rocks



Bulk compositions – problem components

- THERMOCALC uses O to define the amount of Fe_2O_3 , by combining O with 2 lots of FeO in your MOL>% BULK COMPOSITION ($\text{Fe}_2\text{O}_3 = 2\text{FeO} + \text{O}$)
- As there are 2 Fe^{3+} cations in Fe_2O_3 , to get $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.1$, you need to divide your initial FeO content by 20. $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.2$ is FeO/10



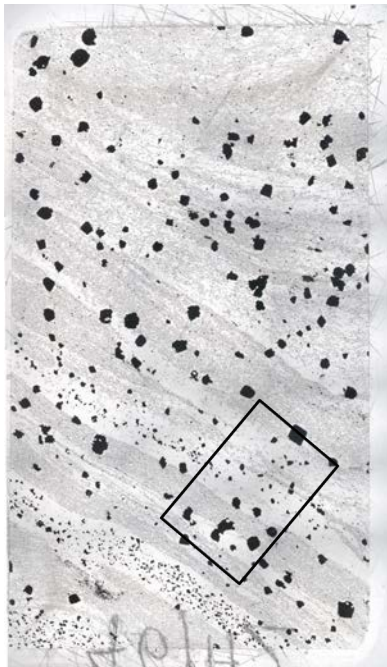
Thermodynamic basics – equilibrium

- The **equilibrium volume** is that volume of the system that has reached equilibrium
- The phases that develop within the equilibrium volume will be a function of P , T and the bulk composition of the equilibrium volume
- A larger equilibrium volume is favoured by high T and the presence of fluids (melts or volatiles) that lead to large diffusional length scales



Thermodynamic basics – equilibrium

- In general, **higher temperatures will lead to larger equilibrium volumes**, such that many high-grade metamorphic rocks can be assumed to have reached equilibrium on a thin-section, hand specimen or even outcrop scale
- However, in rocks that reached $\sim 1100^{\circ}\text{C}$...



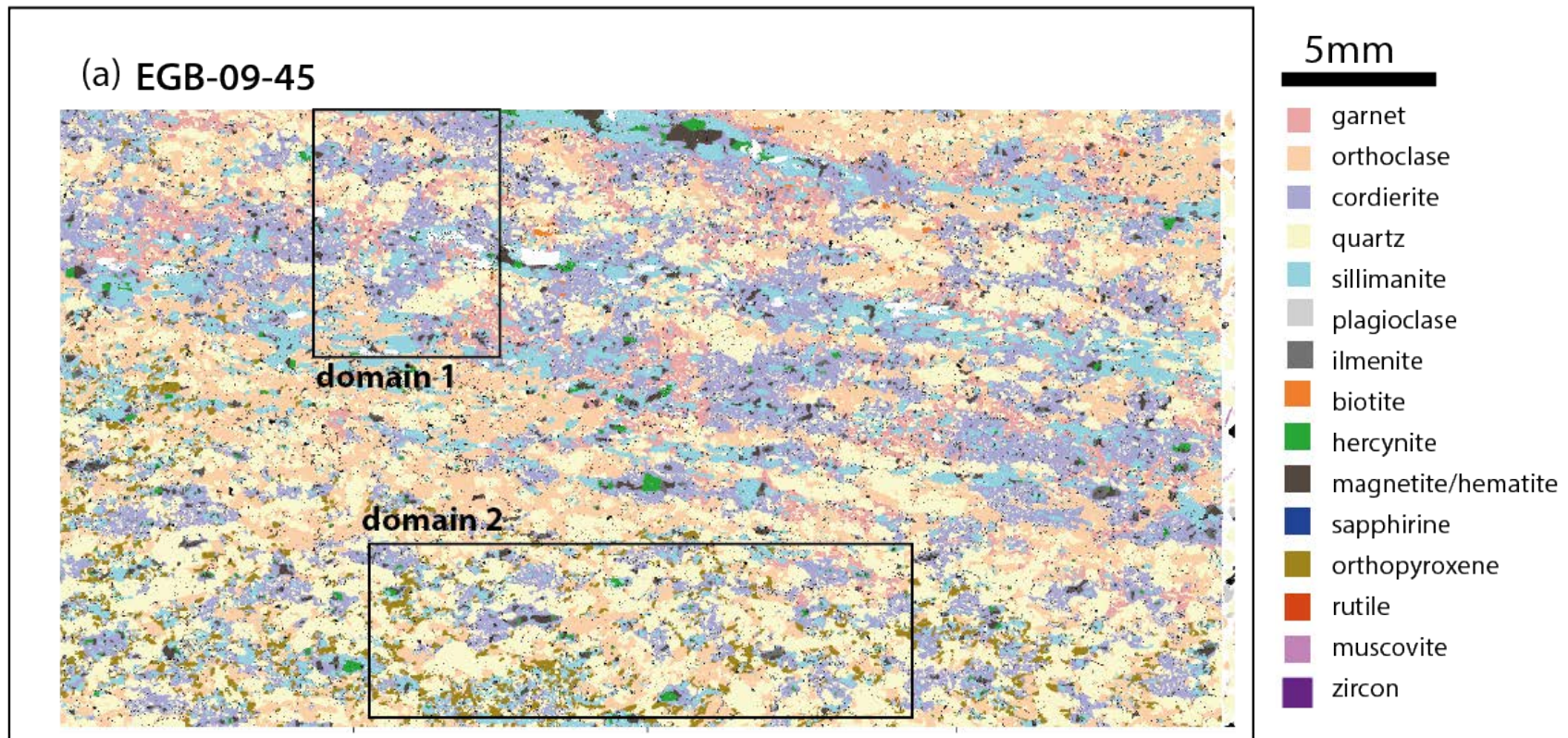
$$\begin{aligned} X_{\text{Mg}}(\text{cd}) &= 0.65 \\ X_{\text{Mg}}(\text{sp}) &= 0.16 \end{aligned}$$



$$\begin{aligned} X_{\text{Mg}}(\text{cd}) &= 0.60 \\ X_{\text{Mg}}(\text{sp}) &= 0.12 \end{aligned}$$

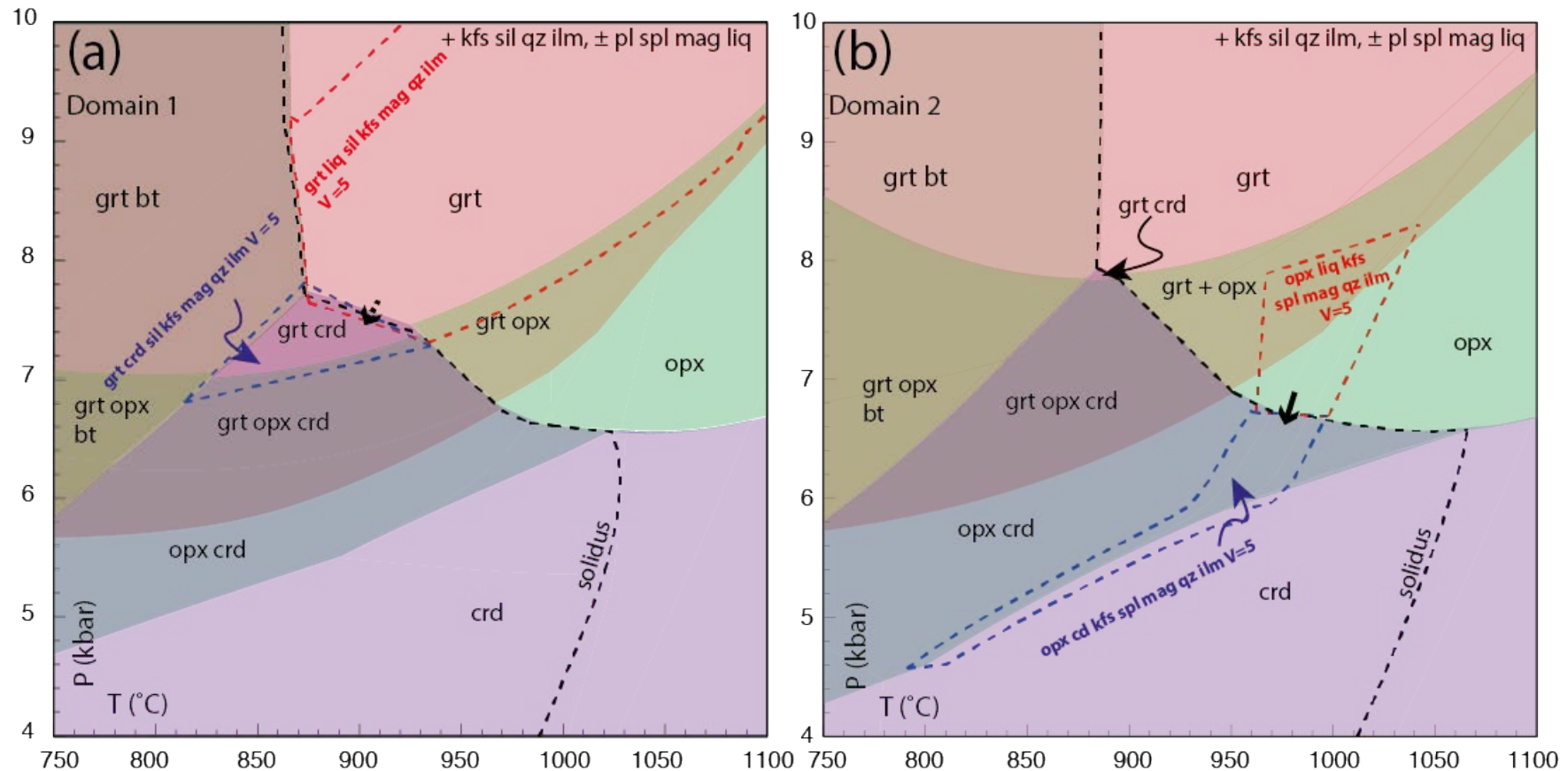


Domainal equilibrium at UHT



- Domains rich in: opx + sill (no g) and g + sill (no opx) did not equilibrate
- Requires calculation of an assumed equilibration volume

Domainal equilibrium at UHT



- The assemblage in the different domains defines overlapping fields
- Late cordierite suggests some minor decompression

Adjusting bulk compositions

- Bulks can be set/adjusted using the mineral modes (mole proportions) and the mineral compositions
- Uses the **rbi code** (rbi = read bulk info) – see web-based tutorial at <http://www.metamorph.geo.uni-mainz.de/thermocalc/tutorials/index.html>
- You can make THERMOCALC output the rbi info into the tc-log.txt file using the command '**printbulkinfo yes**'

=====												
%		liq	ksp	pl	bi	cd	g	ilm	sill	q	mineral modes	
rbi	yes	0.02388	0.03271	0.07669	0.3172	0	0	0.01311	0.1977	0.3388		
%		H2O	SiO2	Al2O3	CaO	MgO	FeO	K2O	Na2O	TiO2	O	
rbi		0.49808	1.6565	0.17949	0.0050594	0.0015289	0.0076801	0.084630	0.065008	0	0	% liq
rbi		0	2.9955	0.50224	0.0044738	0	0	0.41815	0.079615	0	0	% ksp
rbi		0	2.7228	0.63859	0.27718	0	0	0.031436	0.32997	0	0	% pl
rbi		1.0000	2.5183	0.97268	0	0.72478	1.7233	0.50000	0	0.044128	0.0090505	% bi
rbi		0.57016	5.0000	2.0000	0	0.91768	1.0823	0	0	0	0	% cd
rbi		0	3.0000	0.99368	0.087875	0.31250	2.6123	0	0	0	0.0063241	% g
rbi		0	0	0	0	0	1.0657	0	0	0.93434	0.065657	% ilm
rbi		0	1.0000	1.0000	0	0	0	0	0	0	0	% sill
rbi		0	1.0000	0	0	0	0	0	0	0	0	% q
=====												
mineral compositions												

Adjusting bulk compositions

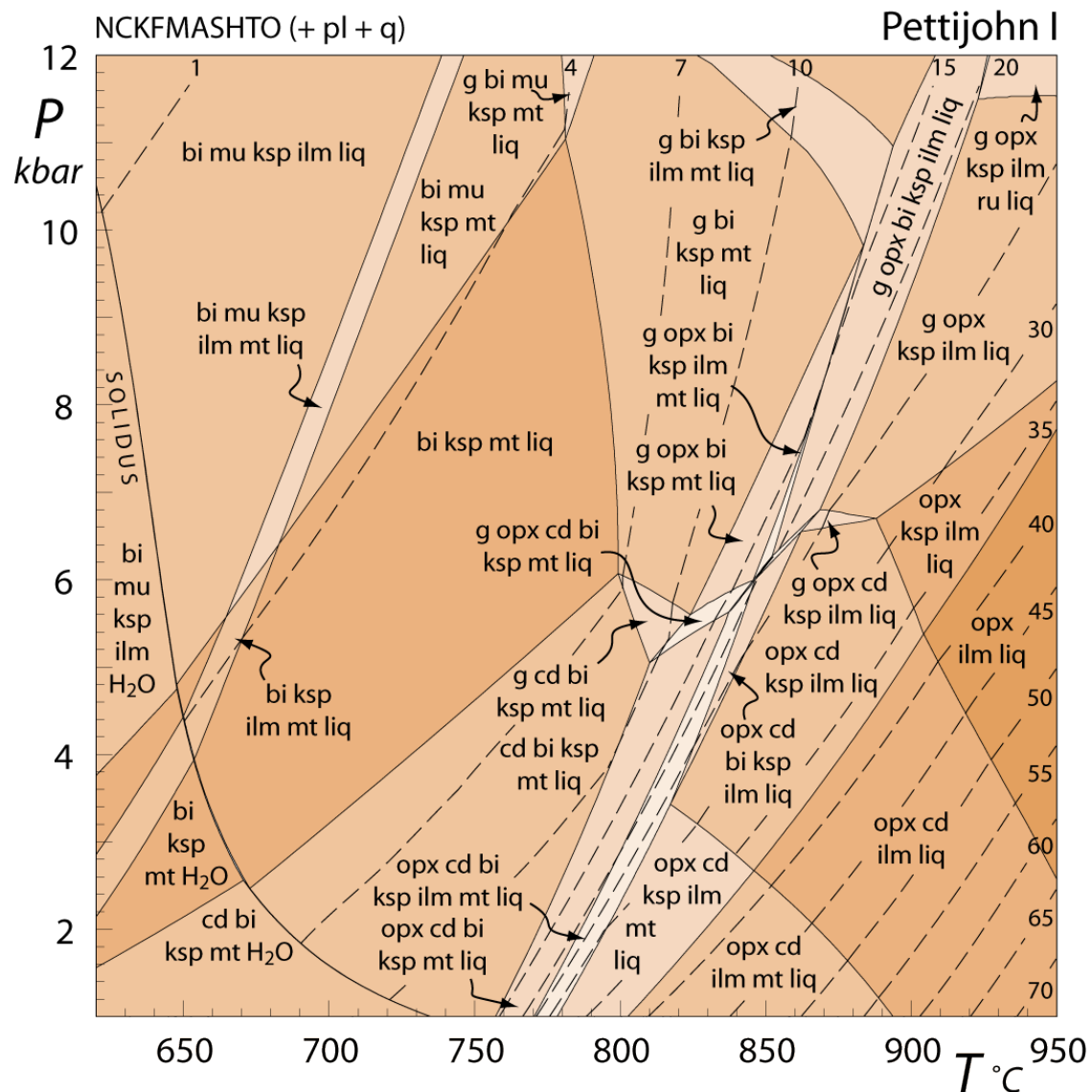
- The bulk rock can be read from rbi code in the script file “tc-blah.txt” instead of the usual mole oxide %s

here I've used rbi to remove melt from a modelled rock composition

```
pseudosection yes
% =====
%      liq      ksp      pl      bi      g      ilm      sill      q
rbi yes      0.00      0.4997      0.02795      0.04152      0.01854      0.001830      0.04876      0.2527

%      H2O      SiO2      Al2O3      CaO      MgO      FeO      K2O      Na2O      TiO2      0
rbi      0.55458      1.4730      0.15744      0.0061140      0.00068111      0.0041943      0.078664      0.055416      0      0      % liq
rbi      0      2.9961      0.50194      0.0038747      0      0      0.43780      0.060261      0      0      % ksp
rbi      0      2.6361      0.68196      0.36393      0      0      0.020277      0.29776      0      0      % pl
rbi      1.0000      2.4695      1.0178      0      0.53815      1.8701      0.50000      0      0.043337      0.012671      % bi
rbi      0      3.0000      0.99053      0.14650      0.21561      2.6568      0      0      0      0.0094682      % g
rbi      0      0      0      0      0      1.1210      0      0      0.87903      0.12097      % ilm
rbi      0      1.0000      1.0000      0      0      0      0      0      0      0      % sill
rbi      0      1.0000      0      0      0      0      0      0      0      0      % q
% =====
% -----
% RH011 xrf composition
% -----
%      H2O      SiO2      Al2O3      CaO      MgO      FeO      K2O      Na2O      TiO2      0
%setbulk yes 11.42 65.15 10.20 0.55 1.10 5.76 4.09 1.58 0.11
% -----
```


Contouring pseudosections



From Johnson *et al.* (2008)

- Pseudosections are more useful when contoured for abundance and/or composition of phases
- Formally, all contouring was done 'by hand', line by line and point by point using the '**setmode**' and '**zeromode**' scripts
- For THERMOCALC users, TCIInvestigator (Pearce *et al.* (2015) has made things MUCH easier...

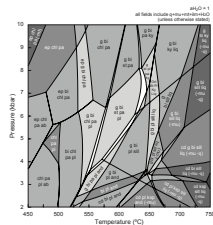
Contouring pseudosections

TCInvestigator: Automated Calculation of Contours for THERMOCALC Pseudosections

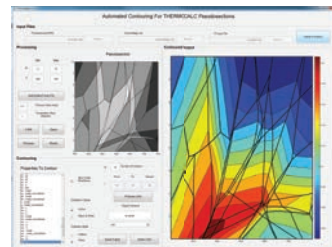
CSIRO Mineral Resources Flagship
www.csiro.au



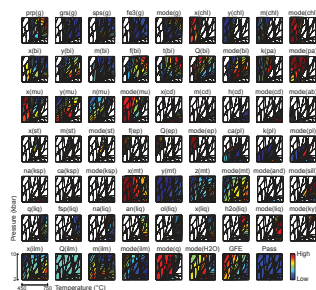
Take a completed THERMOCALC pseudosection and produce contoured plots for all compositional variables and modal proportions



Load pseudosection, script file and assemblage list into the graphical user interface



TCInvestigator



Export contoured plots and values in a range of file types

Download TCInvestigator at:

doi: 10.4225/08/54C99E2D47150



FOR FURTHER INFORMATION CONTACT

Mark A. Pearce

e mark.pearce@csiro.au

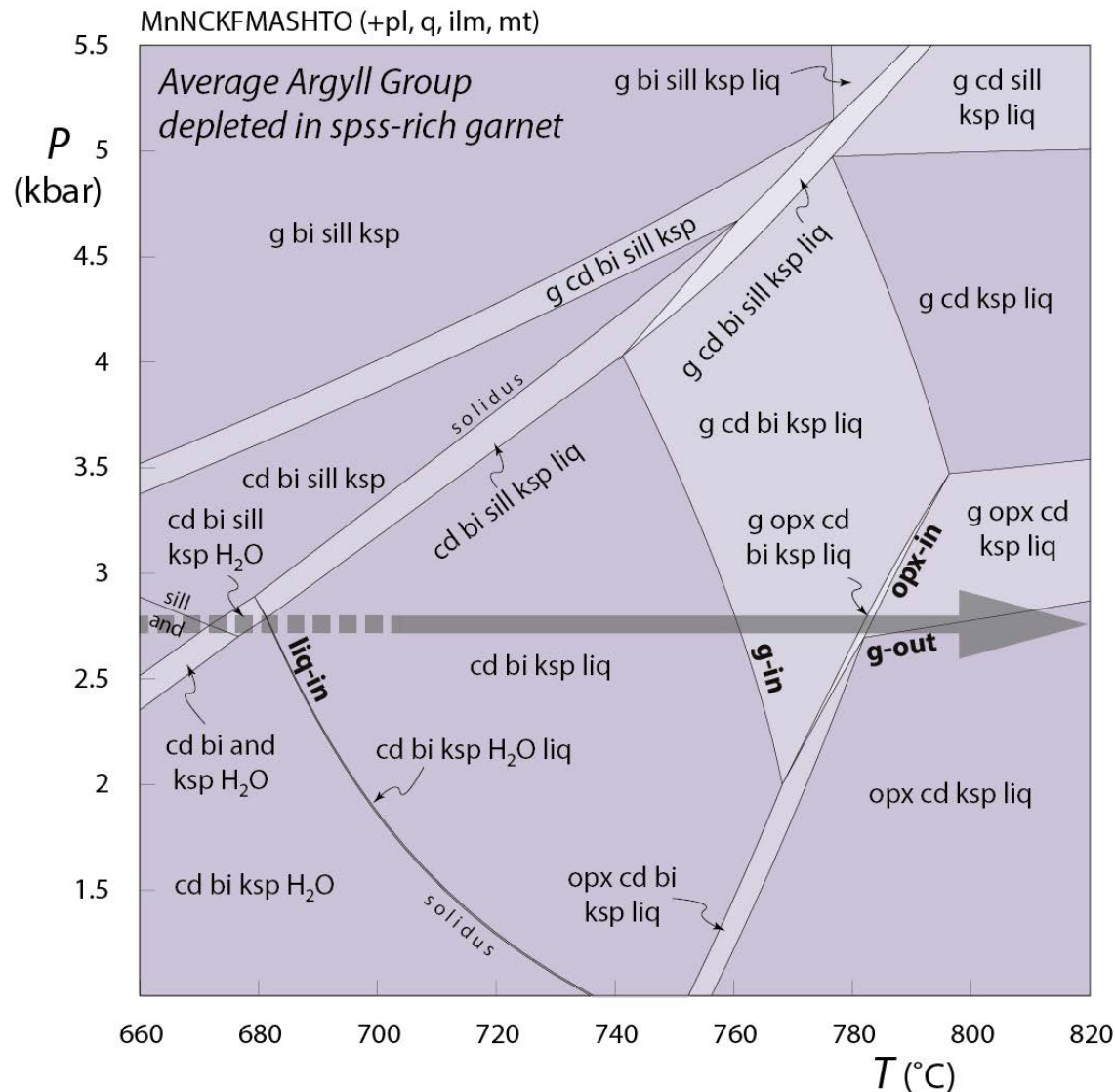
DETAILS PUBLISHED IN

Pearce et al., 2015.

J. Met. Geol., **33**, 413-425, doi: 10.1111/jmg.12126

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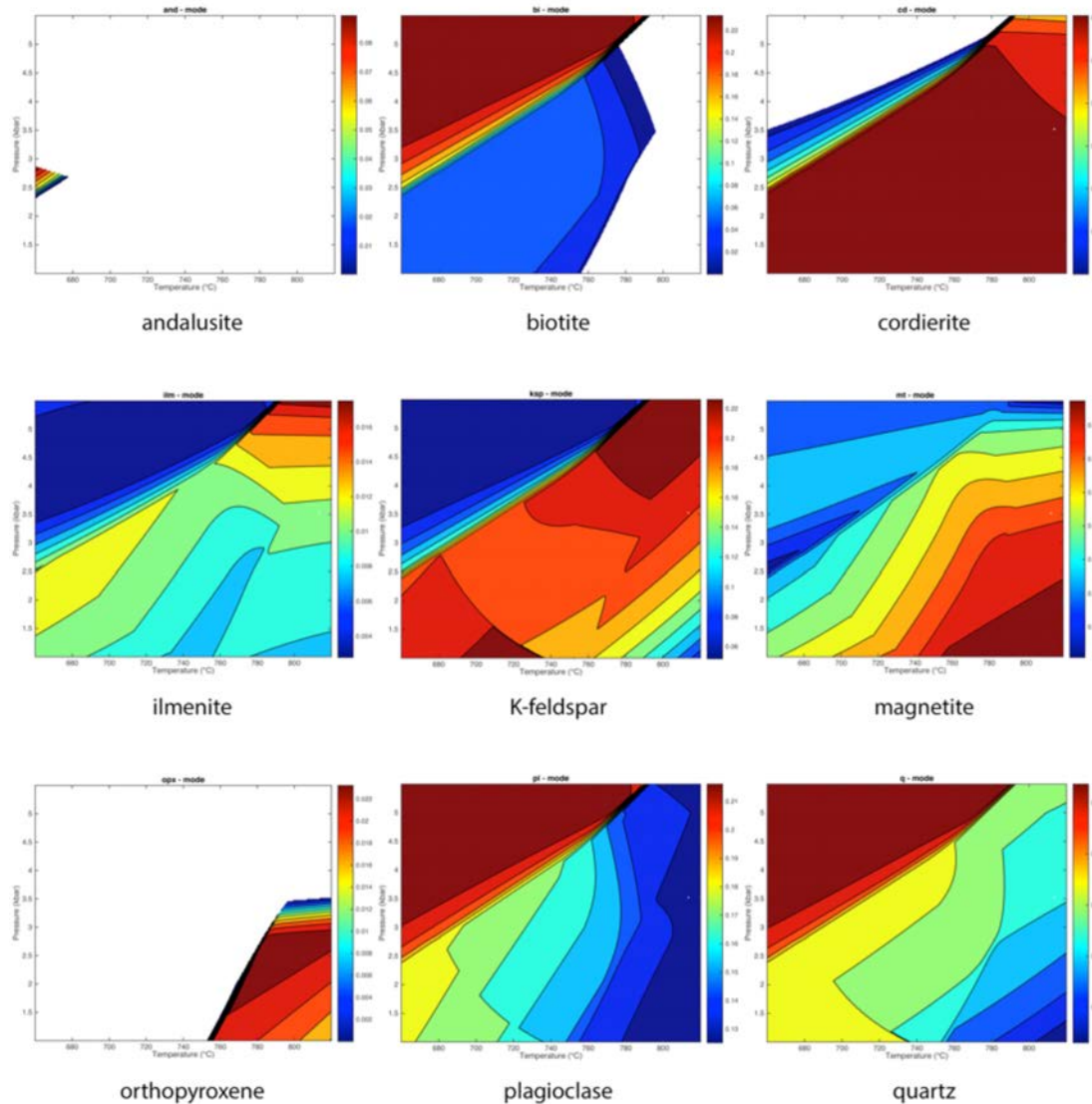
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Contouring pseudosections

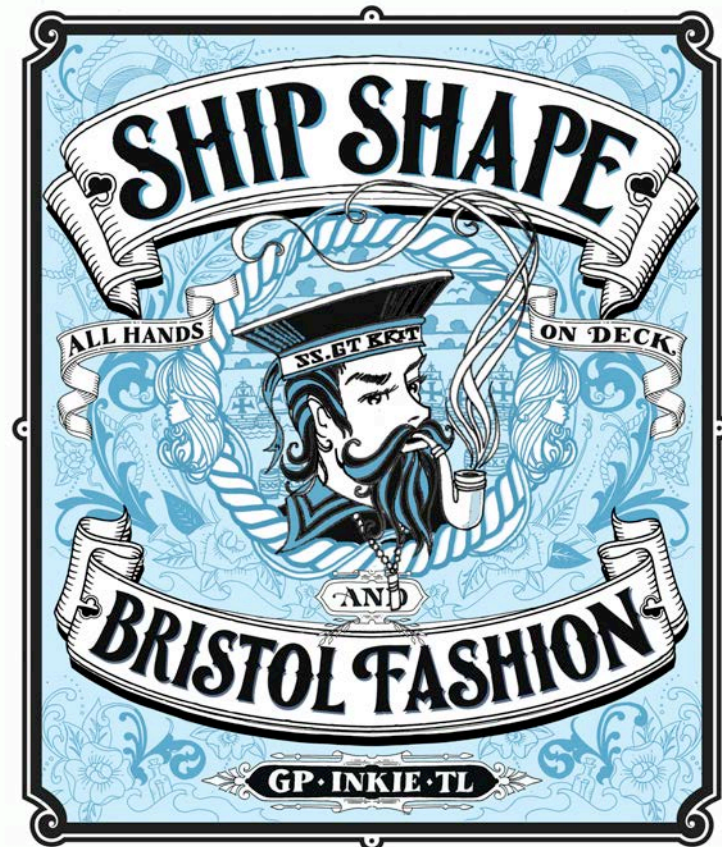


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From Johnson *et al.* (2015)

Getting started

- You can save yourself lots of time by organising your desktop so you can easily navigate between the various applications, windows and files (THERMOCALC and drawpd) you are going to use to both calculate and plot your phase diagram....

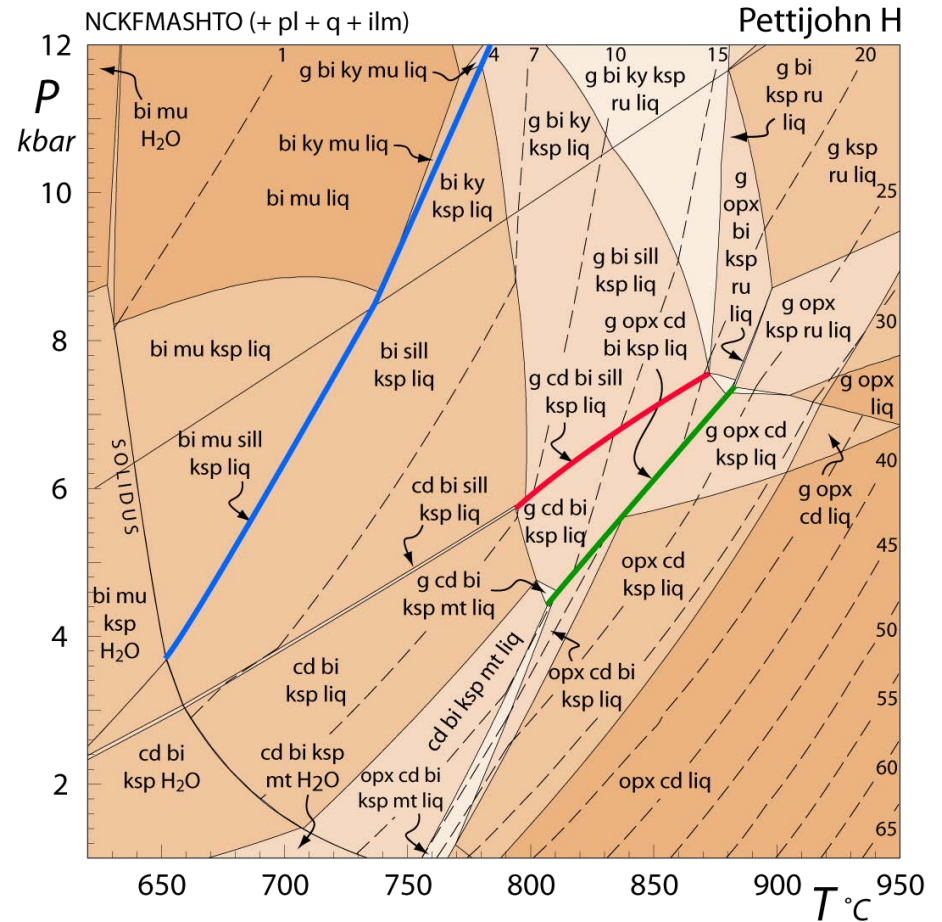


Getting started

- Knowing where to start is not always straightforward
- It is easy to accidentally calculate a metastable higher variance assemblage rather than the stable lower variance one
- Some rocks are dominated by high-variance assemblages in large chemical systems (e.g. greywackes, metabasic rocks)
- There are some smaller system equilibria that form the backbone for larger systems
- In pelitic systems, the classic KFMASH univariant equilibria occur as narrow fields in bigger chemical systems
- NCFMASH univariant equilibria in metabasic rocks may still be there in some form in bigger chemical systems

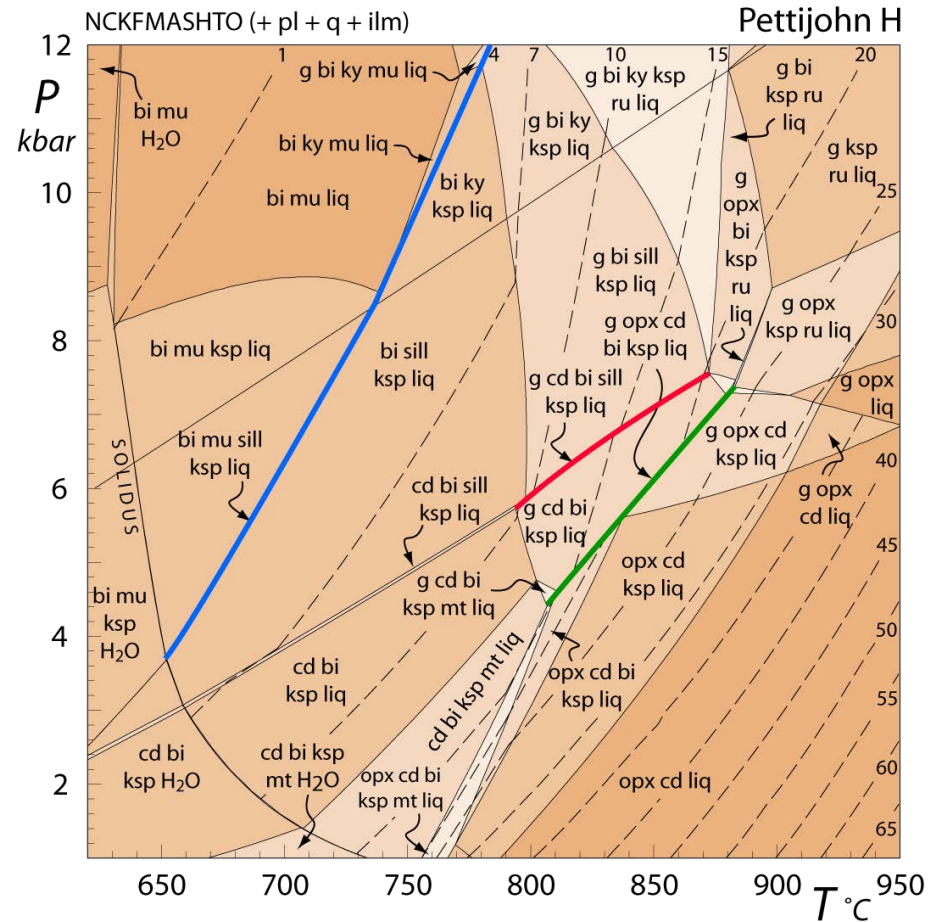
Getting started

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Getting started

- In pelitic systems, the classic KFMASH univariant equilibria occur as narrow fields in bigger chemical systems
- NCFMASH univariant equilibria in metabasic rocks may still be there in some form in bigger chemical systems
- In most cases the broad topology of a pseudosection will be well enough understood that you will know what some of the main equilibria will be (by looking in the literature)



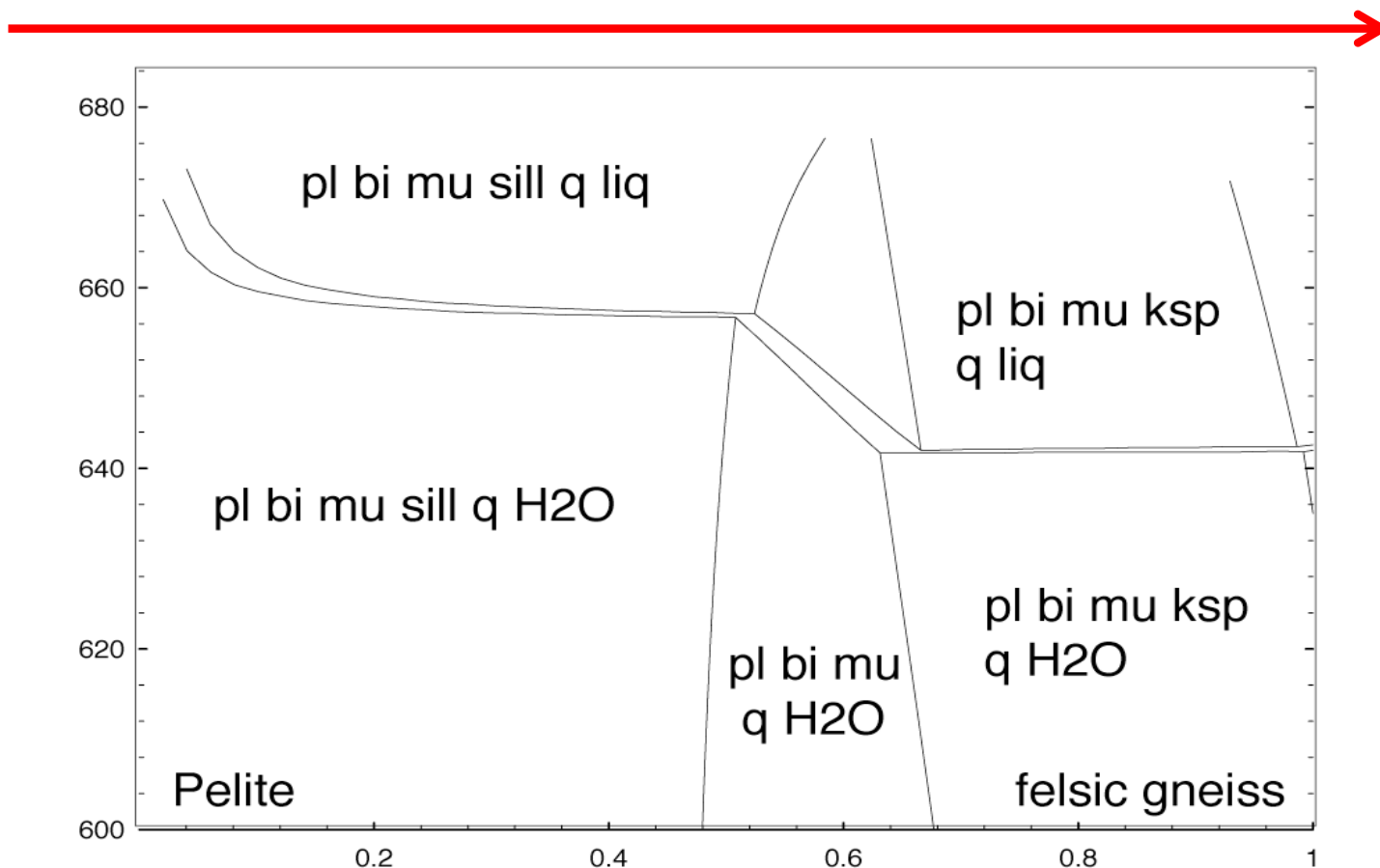
Getting started

If you can't find a boundary to get started, you have two options:

- Calculate part of a T - X or P - X diagram from a known bulk composition ($X = 0$) to your unknown bulk ($X = 1$)
 - Work your way across the diagram, find an equilibria that occurs in your new bulk and build up your P - T pseudosection from there (see Tutorial)
- Use the '**dogmin**' script in to try and find the most stable assemblage at P - T
 - This is a Gibbs energy minimisation method, but may not be reliable

Getting started

Calculate your way across diagram from left to right



P - T pseudosection
known for this
composition

P - T pseudosection
unknown for this
composition

Getting started

```

<=====>
phases : liq, bi, cd, g, ksp, pl, mt, q, H2O, (ilm) or [and]
<== nothing found ==>

<=====>
phases : liq, bi, cd, g, ksp, pl, and, q, H2O, (ilm) or [mt]
<== nothing found ==>

<=====>
phases : liq, bi, cd, g, ksp, mt, and, q, H2O, (ilm) or [pl]
<== nothing found ==>

<=====>
phases : liq, bi, cd, g, pl, mt, and, q, H2O, (ilm) or [ksp]
P(kbar)   T(° C)   q(L)   fsp(L)   na(L)   an(L)   ol(L)   x(L)   h2o(L)   x(bi)   y(bi)   f(bi)   t(bi)   Q(bi)   x(cd)   h(cd)
x(g)      z(g)      f(g)   ca(pl)   k(pl)
2.50      700.0   0.2020  0.2662  0.5529  0.005351  0.001617  0.9751  0.5034  0.9778  0.6390  0.007200  0.06982  0.005263  0.9339  0.4864
0.9904  0.016780 0.0009456  0.3590  0.02207
               x(mt)   y(mt)   z(mt)   x(ilm)   Q(ilm)
               0.9982  0.2126  0.1948  0.8907  -0.8177

<=====>
phases : liq, bi, cd, ksp, pl, mt, and, q, H2O, (ilm) or [g]
P(kbar)   T(° C)   q(L)   fsp(L)   na(L)   an(L)   ol(L)   x(L)   h2o(L)   x(bi)   y(bi)   f(bi)   t(bi)   Q(bi)   x(cd)   h(cd)
na(ksp)   ca(ksp)   ca(pl)   k(pl)   x(mt)
2.50      700.0   0.2423  0.2572  0.2286  0.010200  0.0005283  0.8829  0.4687  0.8358  0.6251  0.01313  0.08482  0.03828  0.6485  0.4864
0.07818  0.008334  0.7474  0.01239  0.9908
               y(mt)   z(mt)   x(ilm)   Q(ilm)
               0.09993  0.1504  0.8230  -0.7300

<=====>
.

```

Always check all of the output carefully especially the compositions of phases (look at starting guesses as well) and use you intuition—does the result look sensible?

Gibbs energy minimisation info

P(kbar)	T(° C)	liq	bi	cd	g	ksp	pl	mt	ilm	and	q	H2O	n	G	del
2.50	700.0	●	●	-	-	●	●	●	●	●	●	-	4	-1045.80957	0.01283

(Use these results at your own risk!)

liq	bi	cd	g	ksp	pl	mt	ilm	and	q	H2O	G	del
0.211	0.234	-	-	0.010	0.003	0.013	0.009	0.309	0.212	-	-1045.80957	-
-	0.073	0.235	-	-	0.204	0.012	0.013	0.240	0.177	0.046	-1045.79675	0.01283
-	0.073	0.235	-	0.204	-	0.012	0.013	0.240	0.177	0.046	-1045.79675	0.01283
-	0.235	-	-	0.103	0.012	0.012	0.009	0.313	0.277	0.037	-1045.76746	0.04212

Sketching your diagram

- It is **very wise indeed** to sketch the diagram as you go
 - No need to make this sketch an in-proportion and precise rendering of the phase diagram-that's what drawpd is for
- The sketch is there to help you draw the diagram and for labelling
 - Very small fields can be drawn bigger than they really are or as separate diagrams
 - Allows you to keep track of what assemblage the labels for 'out/in' lines (u1, u2 etc) and points (i1, i2 etc..) correspond to
 - New drawpd features allow you to colour and dash lines

Orientation of field boundaries

- Most assemblage field boundaries on a pseudosection are close to linear
- Strongly curved boundaries do occur and can be difficult to calculate in one run
- Very steep & very shallow boundaries & reactions can also present problems
 - For shallow boundaries calculate P at a given T
 - For steep boundaries calculate T at a given P

calctatp ask
calctatp yes
calctatp no

You are prompted at each calculation
You input P to get T
You input T to get P

Starting guesses

- THERMOCALC uses the starting guesses in the *a-x* file “tc-system.txt” as a point from which to begin the (iterative) calculation.
 - ‘Starting guesses’ refers to values for the compositional variables of solid solution phases, e.g. $x(\text{bi})$, $y(\text{bi})$, $q(\text{L})$, $y(\text{opx})$, $x(\text{cd})$, $z(\text{g})$ etc...
- These starting guesses have to:
 - Be reasonably close to the actual calculated results
 - Have common exchange variables in the right order for the minerals e.g. $X_{\text{Fe}} \text{g} > \text{bi} > \text{cd}$
- As the phase diagram calculations proceed, the starting guesses in the *a-x* file may no longer be useful
 - i.e. lines and/or points might cease to calculate in a part of the diagram

Starting guesses

- This may mean having to *change the starting guesses* to calculate different parts of the diagram
- Thankfully, when changing starting guesses, the *a-x* file “tc-system.txt” does **not** have to be modified
- Instead, there is a script/function (‘**printxyz yes**’) that appears in the script file “tc-blah.txt” that tabulates the compositional variables from all solid-solution phases used in the most recent calculation
- The tabulated compositional variables can be found in the “**tc-log.txt**” file

Starting guesses

- These tabulated compositional variables can copied and pasted to the “tc-blah.txt” script file (above the *) – these values become the starting guesses for the for the next calculation
- In this way, every time you need to update the starting guesses, the *a-x* file remains unchanged (you should never need to modify it) and the script file (“tc-blah.txt”) is the only input file that is changed.
- The script ‘**readxyz yes**’ in the script file reads the tabulated starting guesses you pasted in
- Using the most recently output compositional variables is a good way to ensure starting guesses are appropriate for the next/future calculations

Starting guesses

```
% -----
% at P = 8.7, T = 870, for: bi g opx ksp pl mt ilm sill q with g = 0
% -----
ptguess 8.7 870
% -----
xyzguess x(bi)          0.158272
xyzguess y(bi)          0.280595
xyzguess f(bi)          0.0791040
xyzguess t(bi)          0.165881
xyzguess Q(bi)          0.145927
xyzguess x(g)           0.369423
xyzguess z(g)           0.0207947
xyzguess f(g)           0.0135418
xyzguess x(opx)         0.228604
xyzguess y(opx)         0.155044
xyzguess N(opx)         0.206365
xyzguess f(opx)         0.0219122
xyzguess na(ksp)        0.231015
xyzguess ca(ksp)        0.0218892
xyzguess ca(pl)         0.440472
xyzguess k(pl)          0.0488462
xyzguess x(mt)          0.829984
xyzguess y(mt)          0.0927136
xyzguess z(mt)          0.0240336
xyzguess x(ilm)         0.247730
xyzguess Q(ilm)         1.17633e-5 range -0.800 0.800
xyzguess f(sill)        0.00847350
% -----
```

- Every time starting guesses need to be updated, simply paste the new table of variables above the previous/older ones in the tc-blah.txt script file and type a * between the tables. This will make the older unreadable by THERMOCALC (anything below the * is storage and not read).