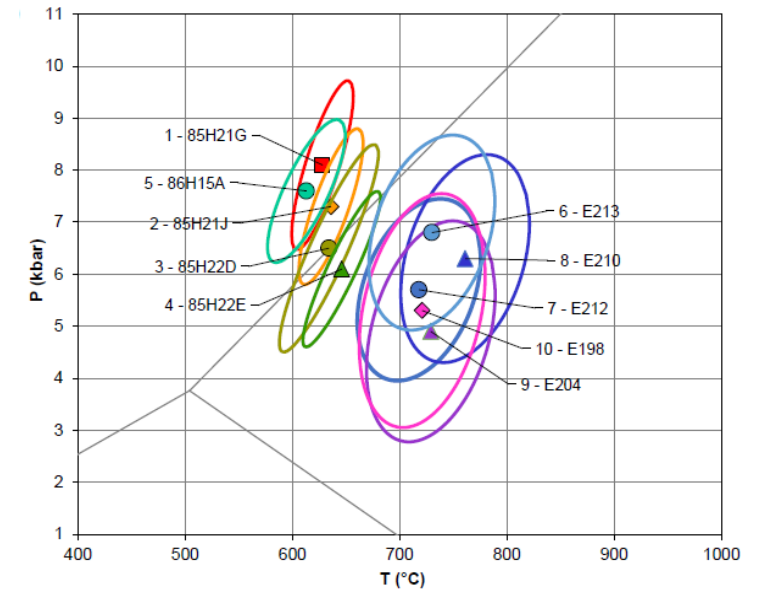


# THERMOCALC & average *P-T*

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# Introduction to THERMOCALC

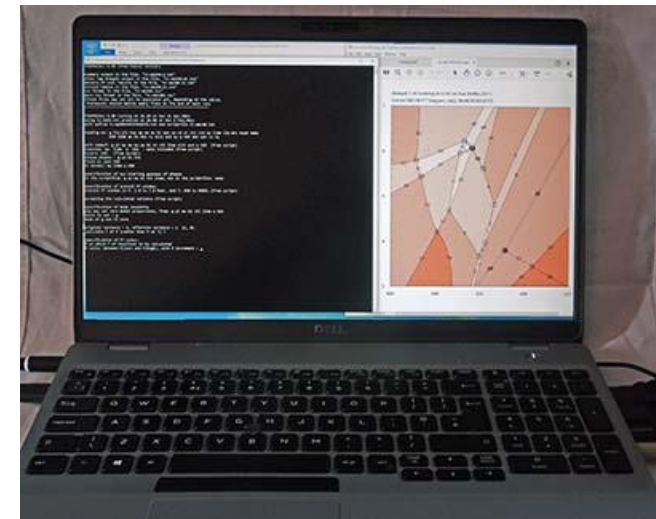
- Origins and landmarks ...
  - Roger Powell doctoral thesis 1973, suite of FORTRAN programs on University mainframe.
  - Holland & Powell 1985 – 1990: internally consistent thermodynamic datasets
  - THERMOCALC release 1988, calculating reactions, average  $P$ - $T$ , uncertainties
  - Pseudosections: DS4, 1990; DS5, 1998  
Powell, Holland & Worley 1998, Calculating phase diagrams
  - THERMOCALC v3.0 onwards, 2001; Improved functionality, DRAWPD, melt models, etc.
  - Dataset 6, Holland & Powell 2011; major revision
  - Expanded solution models, for metapelitic and metabasic systems, 2014 onwards
  - THERMOCALC v3.50: current version, with enhancements and changes to file formats and scripting

Interacting with THERMOCALC through the ages:

1974: TC v.1



1988: TC v.2



2021: TC v.3.50



# Information about THERMOCALC

THERMOCALC program is intimately linked to the Holland & Powell datasets and solution models.

- Website: <https://hpxeosandthermocalc.org/>
- Discussion: <https://groups.io/g/hpxeosandthermocalc>

These sites describe and discuss the current versions and best practice.

Source code is not available

Some users still deploy older versions, datasets and models

- Legacy materials:
  - Official website was at University of Mainz, Germany
  - Documentation from various workshops (2001, 2006, 2009)

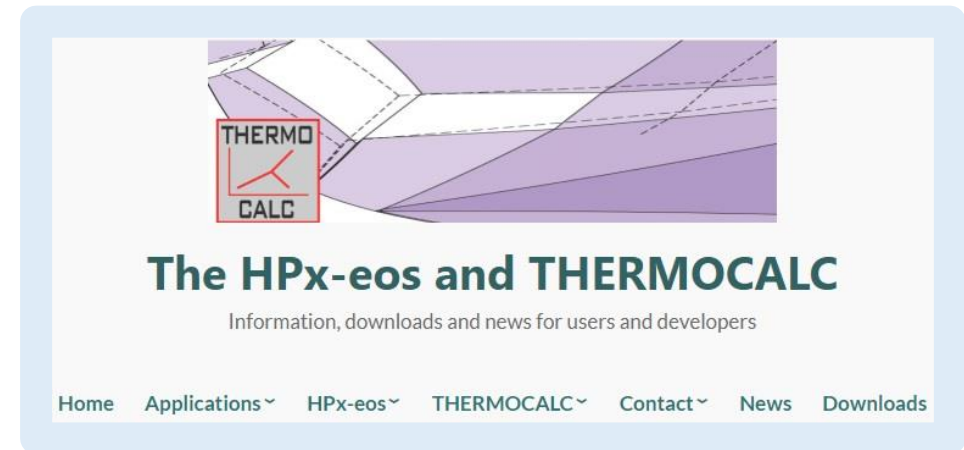
Useful links to older information and archived documents:

[https://serc.carleton.edu/research\\_education/equilibria/index.html](https://serc.carleton.edu/research_education/equilibria/index.html)

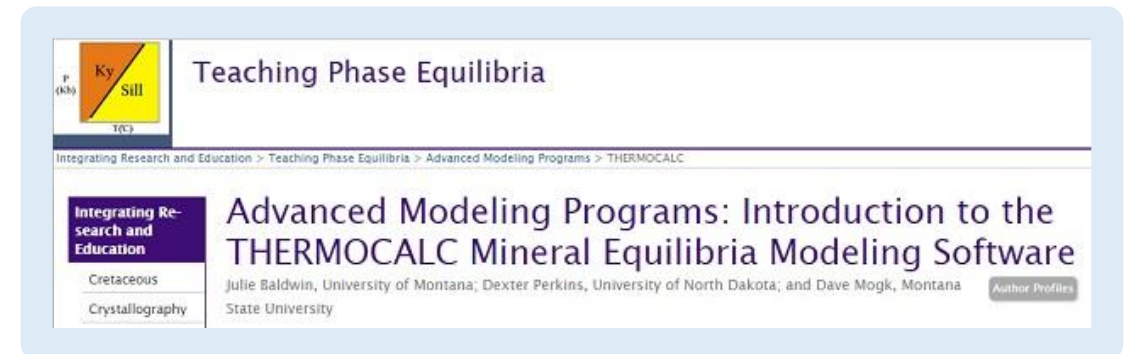
[https://serc.carleton.edu/research\\_education/equilibria/thermocalc.html](https://serc.carleton.edu/research_education/equilibria/thermocalc.html)

[http://serc.carleton.edu/files/research\\_education/equilibria/thermocalc\\_16.pdf](http://serc.carleton.edu/files/research_education/equilibria/thermocalc_16.pdf)

<https://hpxeosandthermocalc.org/>



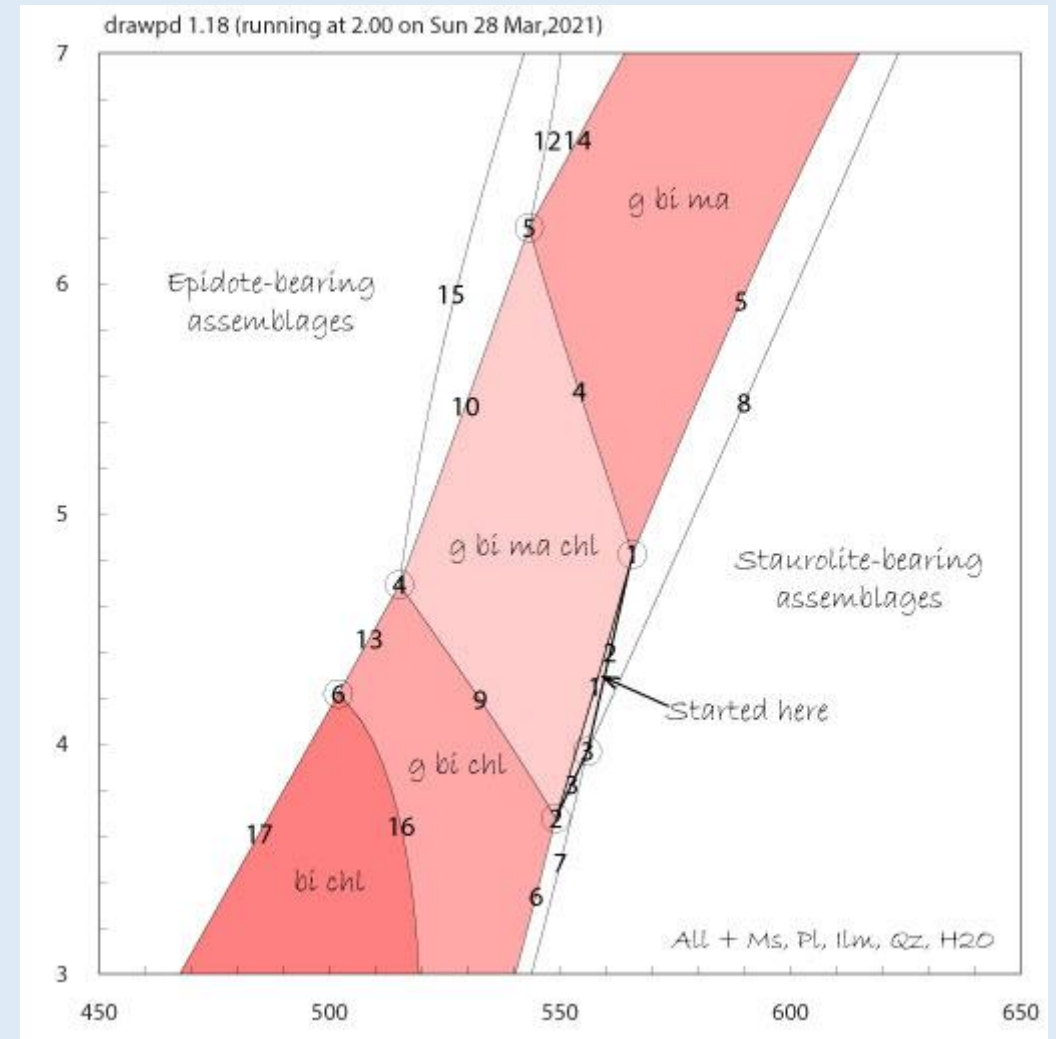
[https://serc.carleton.edu/research\\_education/equilibria/thermocalc.html](https://serc.carleton.edu/research_education/equilibria/thermocalc.html)



# How does it work?

- Algebraic, non-linear equation solver
  - Requires starting guesses for key composition variables
- Principle: from viewpoint of phase diagram construction ...
  - Free-energy minimization: boundaries interpolated
  - **THERMOCALC: boundaries calculated directly**
- Method: Calculates individual equilibria of specified variance
  - **Focus is on lines and points**, e.g. assemblage field boundaries, univariant reactions, invariant intersections
  - **Build up diagram incrementally**, with many short program runs.
- THERMOCALC has three *PTX* calculation modes:
  1. Phase diagram calculations
  2. Rock calculations – average *P-T*
  3. Calculate all reactions in a system

Partially completed metapelite P-T diagram, lines and fields ...







# THERMOCALC output files

## Basic output text files, prefix 'tc-'

- tc-log – almost everything that you see on screen, with your interactive input
- Suffix ‘-o’ – the results of calculations – a subset of what appeared on the screen, minus the interaction
- Suffix ‘-dr’ – a file for use, after editing, with the graphics accessory program DRAWPD

TC350 introduces further output:

- ‘-it’ – solution model coding for phases used in the calculations
- ‘-ic’ – full listing, for each individual calculation, of phase compositions and proportions, site fractions, thermodynamic properties of phases and end members (see later)

### Example of '-o' output file for an assemblage field corner ...

THERMOCALC 3.50 running at 13.53 on Sat 27 Mar,2021  
using tc-ds62.txt produced at 20.08 on Mon 6 Feb,2012  
with axfile tc-mp50MnNCKFMASHT0.txt and scriptfile tc-me148.txt

fluid is just H<sub>2</sub>O

composition (from bulk script)

H2O	SiO2	Al2O3	CaO	MgO	FeO	K2O	Na2O	...	...
20.000	49.859	12.756	2.958	3.541	5.361	2.558	1.992	...	...

<=====>

```
phases: g pl ma bi st chl ilmm (mu, q, fluid)
```

.....

P(kbar)	T(iC)	x(g)	z(g)	m(g)	f(g)	ca(pl)	...	...
4.823	565.70	0.8605	0.08082	0.1817	0.02022	0.4000	...	...
		y(mu)	f(mu)	n(mu)	c(mu)	x(bi)	...	...
		0.9755	0.005148	0.2887	0.02197	0.5508	...	...
		f(st)	t(st)	x(chl)	y(chl)	f(chl)	...	...
		0.07028	0.04023	0.4449	0.6682	0.1638	...	...

mode	g	pl	ma	mu	bi	st	chl
	0.008139	0.1928	0.09345	0.2020	0.2081		
	0.009280	0.2198	0.1065	0.2303	0.2372		

[illegible]

# Database and solution models

- Holland & Powell databases
  - DS5 – latest main revision Sept 2004
  - DS6 – released 2011, major changes from DS5
- Solution models
  - Now re-branded as **HPx-eos**
  - Exist as packages of internally consistent models, cannot be mixed or modified without possibly compromising the database
  - Each solution phase described by an independent set of **'xyz' composition parameters**

## Example (garnet) of how models are coded

Macroscopic end members (5) are pyrope, almandine, spessartine, grossular, khohorite ( $\text{MgFe}^{3+}$ )

'xyz' definitions (4):

$$x(g) = x\text{FeX} / (x\text{FeX} + x\text{MgX})$$

$$z(g) = x\text{CaX}$$

$$m(g) = x\text{MnX}$$

$$f(g) = x\text{Fe3Y}$$

Coding for proportion of pyrope in garnet:

p(py)	3	1	1	4	-1	f	-1	m	-1	x	-1	z
	2		0	1	1	m		0	1	1	x	
	2		0	1	1	x		0	1	1	z	

Coding for occupancy of Mg in X site:

xMgX	3	1	1	3	-1	m	-1	x	-1	z
	2		0	1	1	m	0	1	1	x
	2		0	1	1	x	0	1	1	z

Coding for thermodynamic mole fraction of pyrope in garnet:

py	1	2	xMgX	3	xAlY	2
----	---	---	------	---	------	---



# Propagation of uncertainties

- Propagation of uncertainties
  - Was built in from the outset, based on least-squares regression of fundamental dataset enthalpies, together with their covariances (Powell & Holland, 1985)
  - Generalised procedure for estimating uncertainties on activities from solution model parameters (Powell et al. 1988; Powell & Holland 2008)
  - This uncertainty is also applied to **average P-T** thermobarometry (see later)
  - Authors are concerned that uncertainties *should not be underestimated*.
- More on this in the *Uncertainties & Best Practice* session

## Examples of how these are presented in output

*[Is not present by default ...*

*Switched on using the script 'calcsdnle yes'*

*I recommend that you do this]*

At invariant point (ma,st) in ME148 metapelite

For P, T and composition parameters:

	P(kbar)	T(°C)	x(g)	z(g)	m(g)	f(g)	...
	3.676	549.07	0.8753	0.07280	0.2433	0.01708	...
sd	0.6	13	0.00535	0.00805	0.0475	0.00262	...

... and for modal proportions:

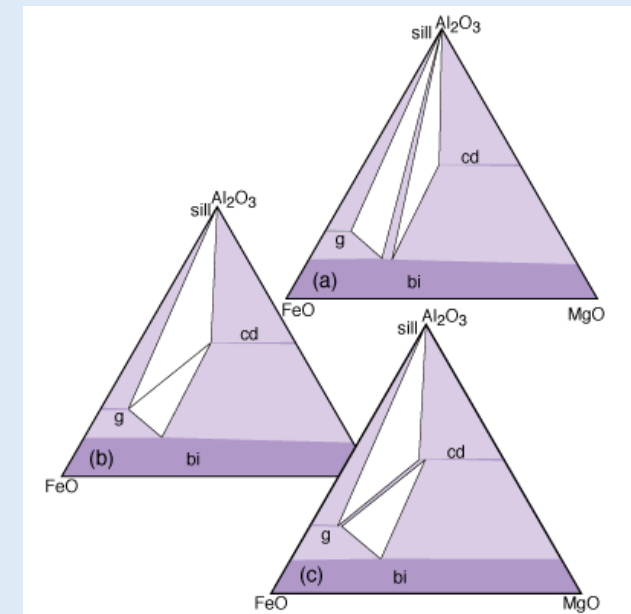
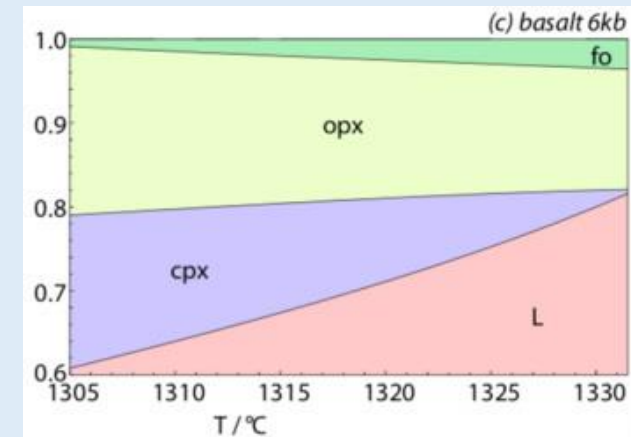
	Mode	g	pl	ma	mu	bi	st	...
		0.004553	0.2831	-	0.2936	0.1693	-	...
sd		0.00142	0.00127	0.00242	0.00385	0.00174	6.14e-5	...



# Calculation types, diagrams

- ***P-T* projections** (petrogenetic grids)
- **Phase diagram** (pseudosection) calculations:  
bulk composition(s) required;  
includes all variations of *P-T-X* diagram type
- Data for **modeboxes** (in tc350)
- **Compatibility diagrams** (composition projections)
  - Is described in older documentation
  - New features for tc350 (Simon Schorn tutorial, see download link on 'compatibility diagrams' website page)
- **Free energy minimization** (*dogmin*)

Examples: 'modebox' and compatibility diagrams



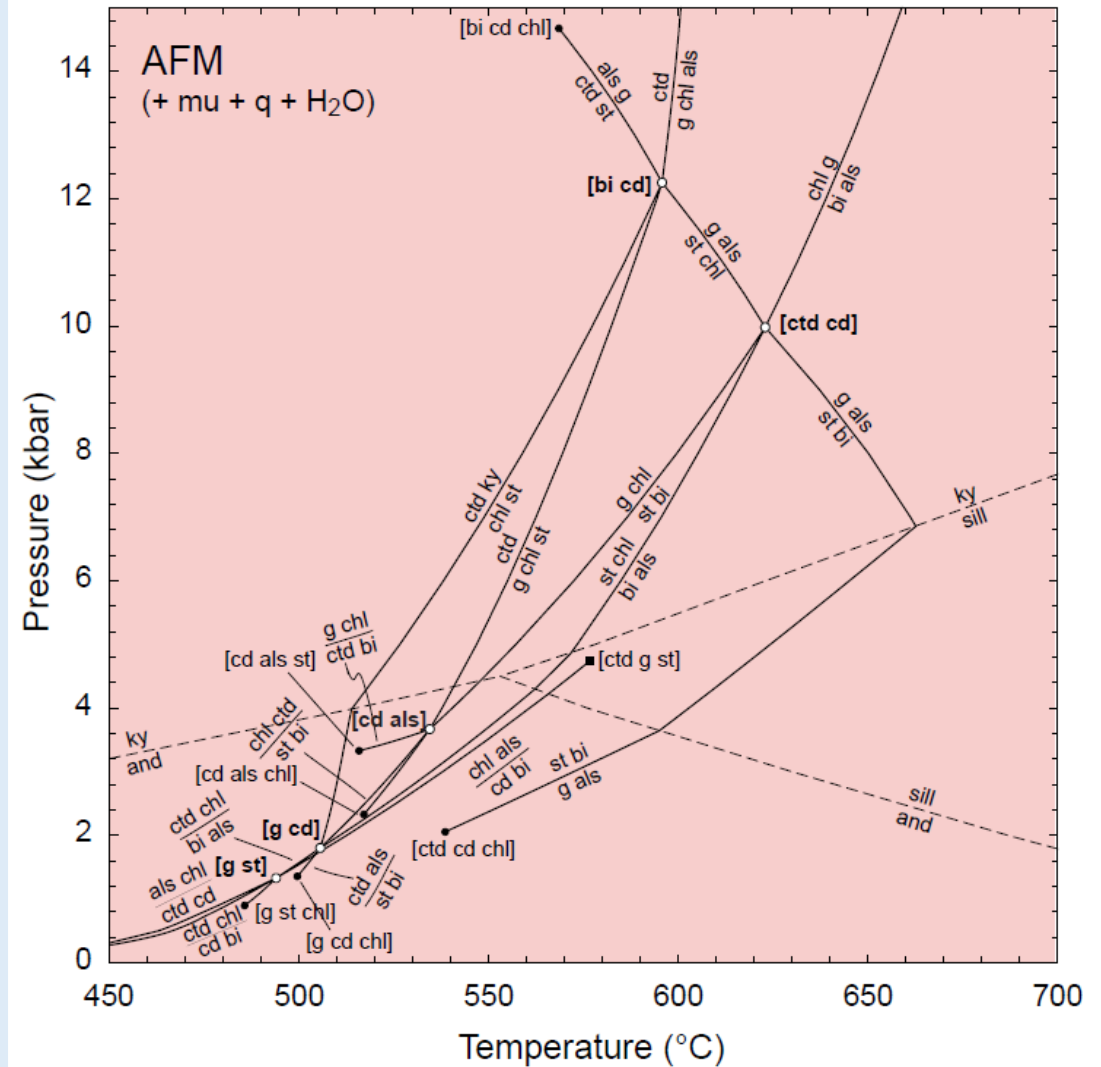
# P-T projection

- Shows all stable reaction curves and invariants, regardless of bulk composition
- Helpful for simple systems
- Gets very complex for large systems

Example: Classic KFMASH metapelite grid, from old THERMOCALC documentation.

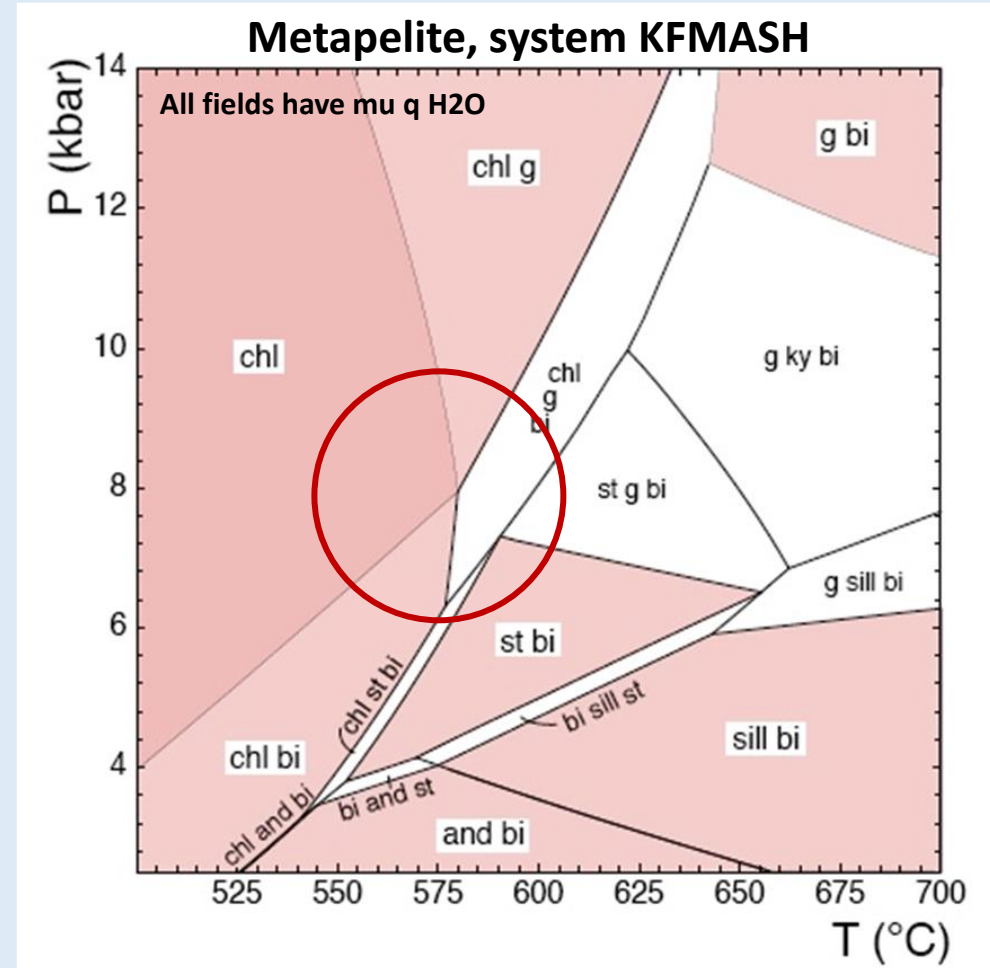
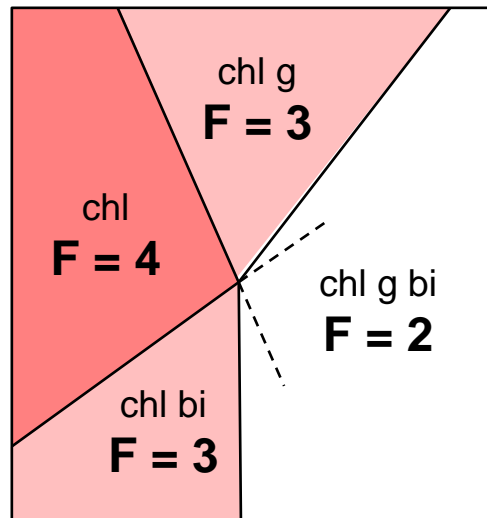
- Diagram consists of linked bundles of stable reaction curves arranged according to Schreinemakers' rules
- Note some curves terminate in simpler end-member systems

As for all applications of THERMOCALC, the user must be familiar with the geometrical properties of phase diagrams, e.g., Schreinemakers' rules



# P-T isochemical phase diagram (pseudosection)

- Script instruction 'pseudosection' calculates relevant information
- Bulk composition entered as oxides, in a specified order.  
Compositions are always normalised to 100 oxide units
- Calculates sections of curves that are 'seen' by the rock composition, i.e., all calculated phase modes are positive or zero
- Geometrical rules for assemblage fields
  - Note changes in no. of phases and assemblage variance
  - Note metastable extensions of high-variance boundaries
  - A univariant curve behaves like an infinitely narrow field with 2 sides



# P-T phase diagram construction (1)

How to start with 'dogmin' – have you included all likely phases? Trade-off between inclusion and long calculation time

- Choose one or more isobaric and isothermal traverses across *PT* box. THERMOCALC cycles through all combinations of phases, from variance 2 to the specified max variance. Identifies lowest *G* at each *PT* point. Output as below.
- Run at a single *PT* point gives further detail, listing equilibria in order of increasing *G*.

Output from isobaric 'dogmin' run, allowing identification of some assemblage boundaries – choose your starting position for the diagram!

A promising area  
to start work? →

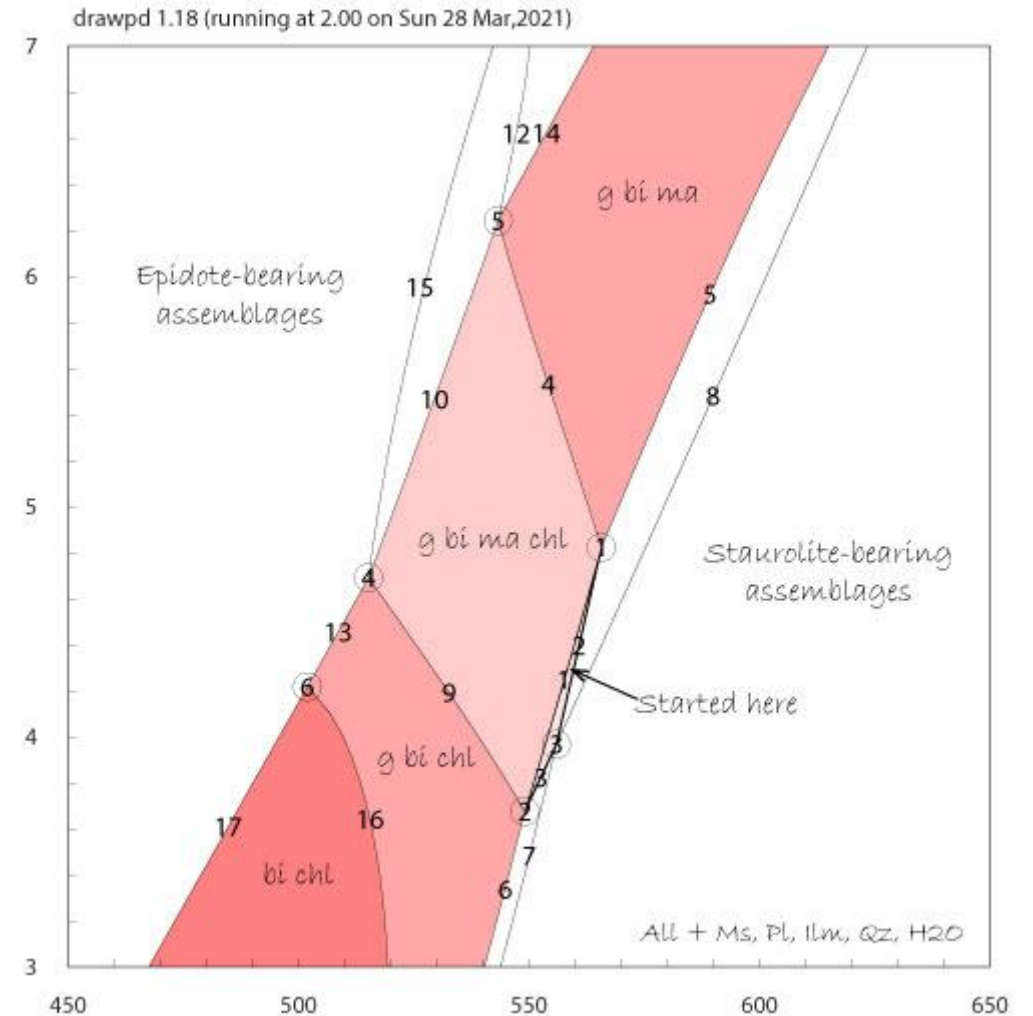
P(kbar)	T(°C)	g	pl	ep	ma	bi	st	chl	ilmm	sill	G	del	n	#
5.000	450.00	.	X	X	.	X	.	X	X	.	-868.36956	0.02212	18	189
5.000	460.00	.	X	X	.	X	.	X	X	.	-869.41418	0.02345	17	189
5.000	470.00	.	X	X	.	X	.	X	X	.	-870.47026	0.02419	17	189
5.000	480.00	.	X	X	.	X	.	X	X	.	-871.53807	0.02558	18	189
5.000	490.00	X	X	X	.	X	.	X	X	.	-872.61798	0.00000	19	244
5.000	500.00	X	X	X	.	X	.	X	X	.	-873.71051	0.00005	23	244
5.000	510.00	X	X	X	.	X	.	X	X	.	-874.81623	0.00018	22	244
5.000	520.00	X	X	X	X	X	.	X	X	.	-875.93592	0.00005	22	318
5.000	530.00	X	X	.	X	X	.	X	X	.	-877.07009	0.00049	20	254
5.000	540.00	X	X	.	X	X	.	X	X	.	-878.21466	0.00077	16	254
5.000	550.00	X	X	.	X	X	.	X	X	.	-879.36953	0.00062	15	254
5.000	560.00	X	X	.	X	X	.	X	X	.	-880.53468	0.00003	15	254
5.000	570.00	X	X	.	X	X	X	.	X	.	-881.70998	0.00001	18	252
5.000	580.00	X	X	.	.	X	X	.	X	.	-882.89949	0.00115	13	134
5.000	590.00	X	X	.	.	X	X	.	X	.	-884.10201	0.00093	13	134
5.000	600.00	X	X	.	.	X	X	.	X	.	-885.31376	0.00075	14	134
5.000	610.00	X	X	.	.	X	X	.	X	.	-886.53457	0.00062	13	134
5.000	620.00	X	X	.	.	X	.	.	X	X	-887.76776	0.00155	13	138
5.000	630.00	X	X	.	.	X	.	.	X	X	-889.01115	0.00107	12	138
5.000	640.00	X	X	.	.	X	.	.	X	X	-890.26353	0.00069	11	138
5.000	650.00	X	X	.	.	X	.	.	X	X	-891.52478	0.00041	11	138



# P-T phase diagram construction (2)

- Start from convenient low-variance field, bounded by invariant points (two modes = zero)
- Work outwards along univariant lines (mode of phase = 0), from first invariant points
- Sketch developments with pencil & paper, or paste interim results into a spreadsheet
- Be alert to appearance of new phases – consult *dogmin* run results, or study similar diagrams
- Modify starting guesses as required (paste in output from suitable P,T):

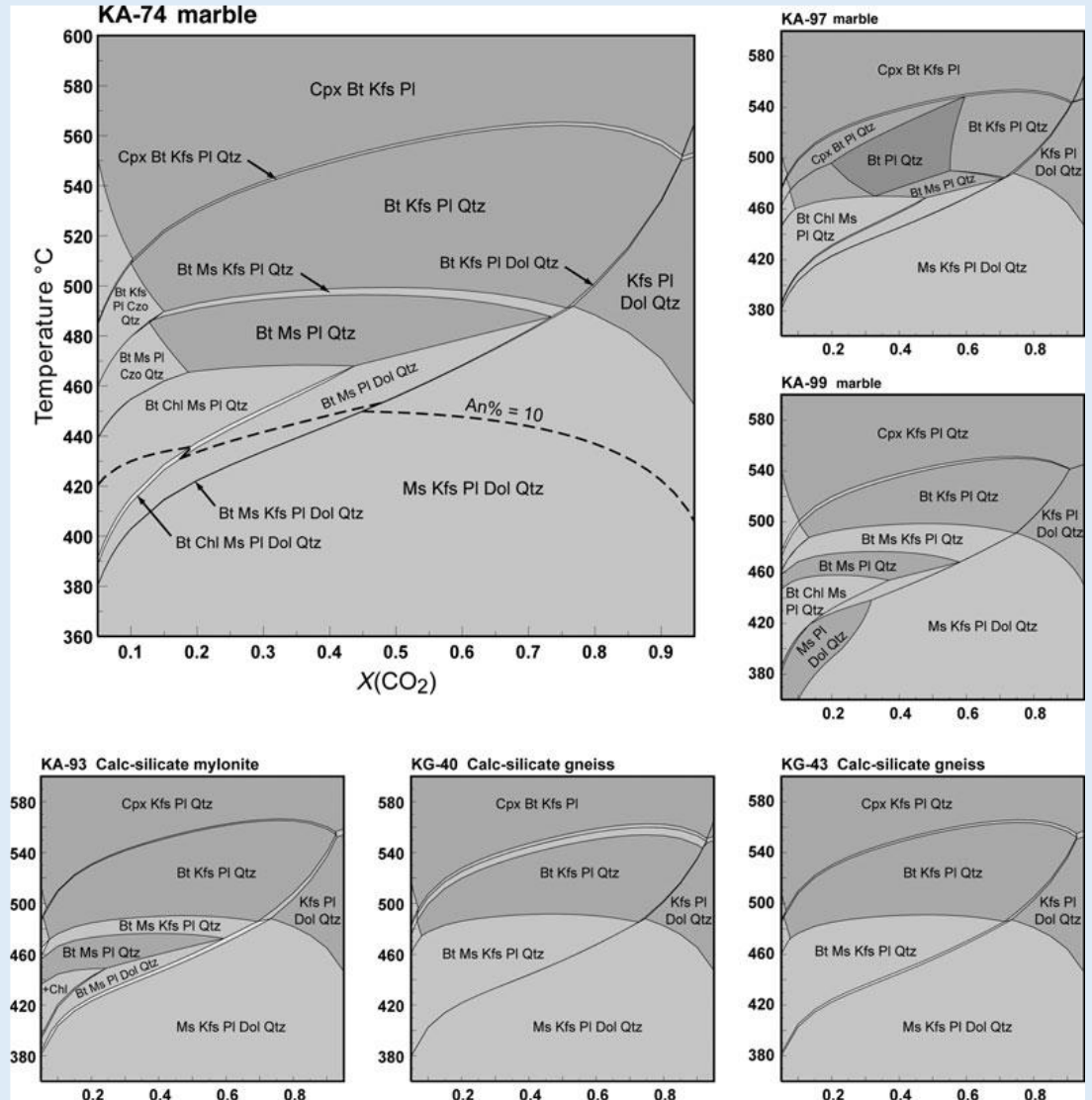
```
% at P = 4.8, T = 566, for: g pl ma mu bi st chl ilmm q ...
% -----
ptguess 4.823 565.70
% -----
xyzguess x(g)      0.860528
xyzguess z(g)      0.0808171
xyzguess m(g)      0.181670
xyzguess f(g)      0.0202180
% -----
xyzguess ca(pl)    0.400009
xyzguess k(pl)     0.00362463
... etc etc
```



# T-X (or P-X) phase diagram (1)

- Where  $X$  is fluid composition, e.g.,  $\text{H}_2\text{O} - \text{CO}_2$ 
    - Calculations performed at specified increments along the  $X$  axis
  - Other examples
    - T-X(Mg) see next slide
    - T-X( $\text{Fe}^{3+}$ ) varying oxidation state of Fe
    - T-M( $\text{H}_2\text{O}$ ) varying moles of  $\text{H}_2\text{O}$
    - T-X(melt) varying proportion of melt
- Last three may be discussed in other sessions, e.g., Friday's topics

T – XCO<sub>2</sub> diagrams at 3 kbar from Cottle et al. 2011 JMG



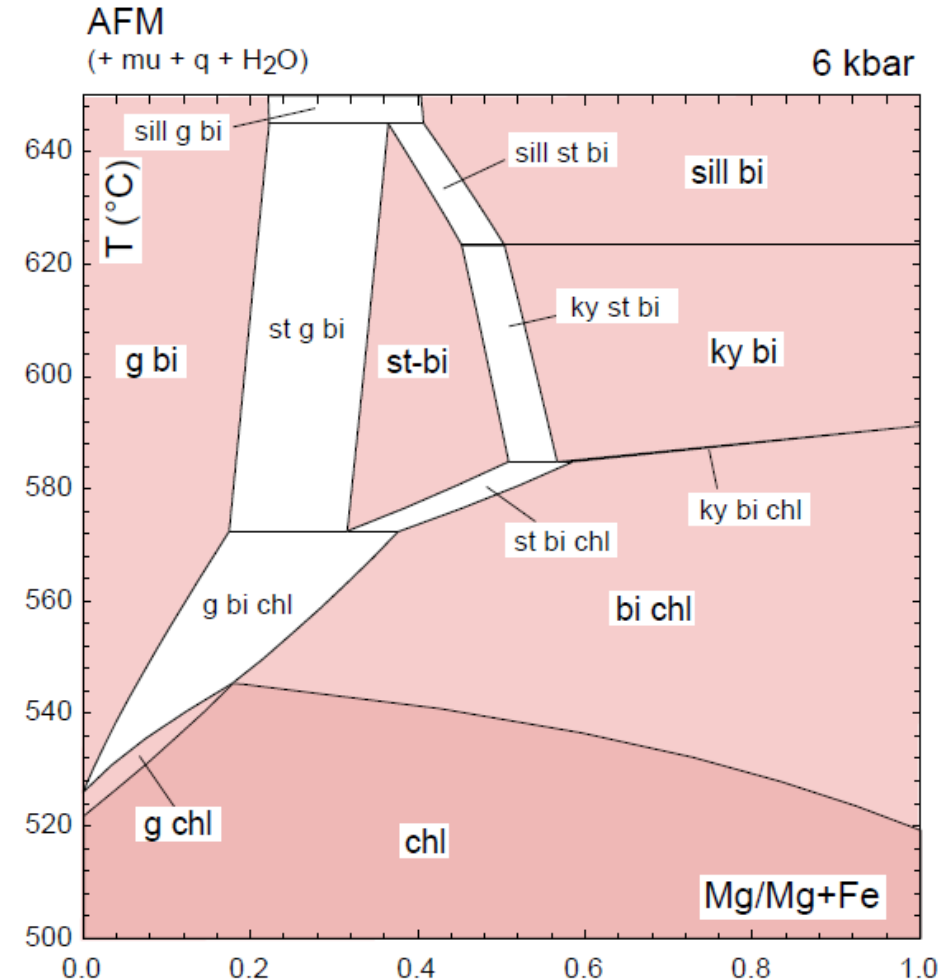


# T-X (or P-X) phase diagram (2)

Where X is a composition variable, e.g., Mg/(Mg+Fe)

- Useful for overview of a system with ferromagnesian phases
- Calculations are made at discrete values of the X-axis
- Not quite so simple to locate invariant points in these cases – requires interpolation

T-XMg diagram, metapelite in KFMASH (Powell et al. 1998)



# Isopleth calculations

... for composition parameters and for modes

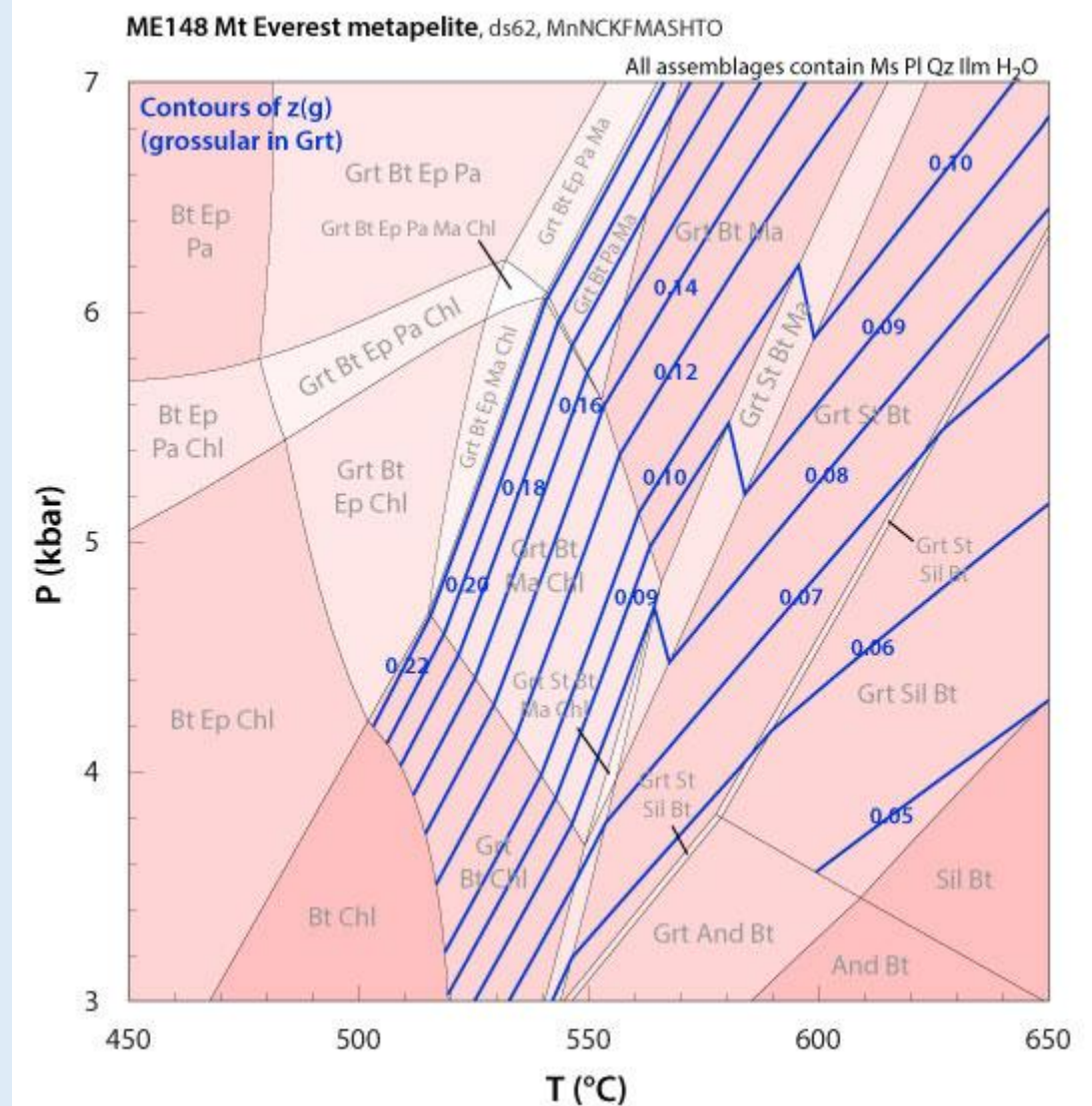
- Each isopleth is treated as a univariant curve
- Each assemblage field must be treated in turn

For 'xyz' composition parameters:

- Use script 'isopleth' ['setiso' prior to tc350]
- Choose parameter from list
- Set range of values and interval
- Intersection between isopleth and a field boundary can be determined by setting, in addition, the relevant phase to zero mode.

Calculating isopleths and organizing data output can be labour-intensive, but for narrow fields, just join matching points on boundaries.

Note that you cannot contour derived parameters, such as  $X(\text{prp})$  in a garnet formulated with  $x(\text{g})$ ,  $z(\text{g})$  and  $f(\text{g})$



# Mode isopleth calculations

- Modes have idiosyncratic units (1-oxide-molar basis), but can be converted to volumes using density or molar volume data
- Mode contouring in THERMOCALC has other issues, including counterintuitive scripting, and normalization effects
  - The “H<sub>2</sub>O effect”:

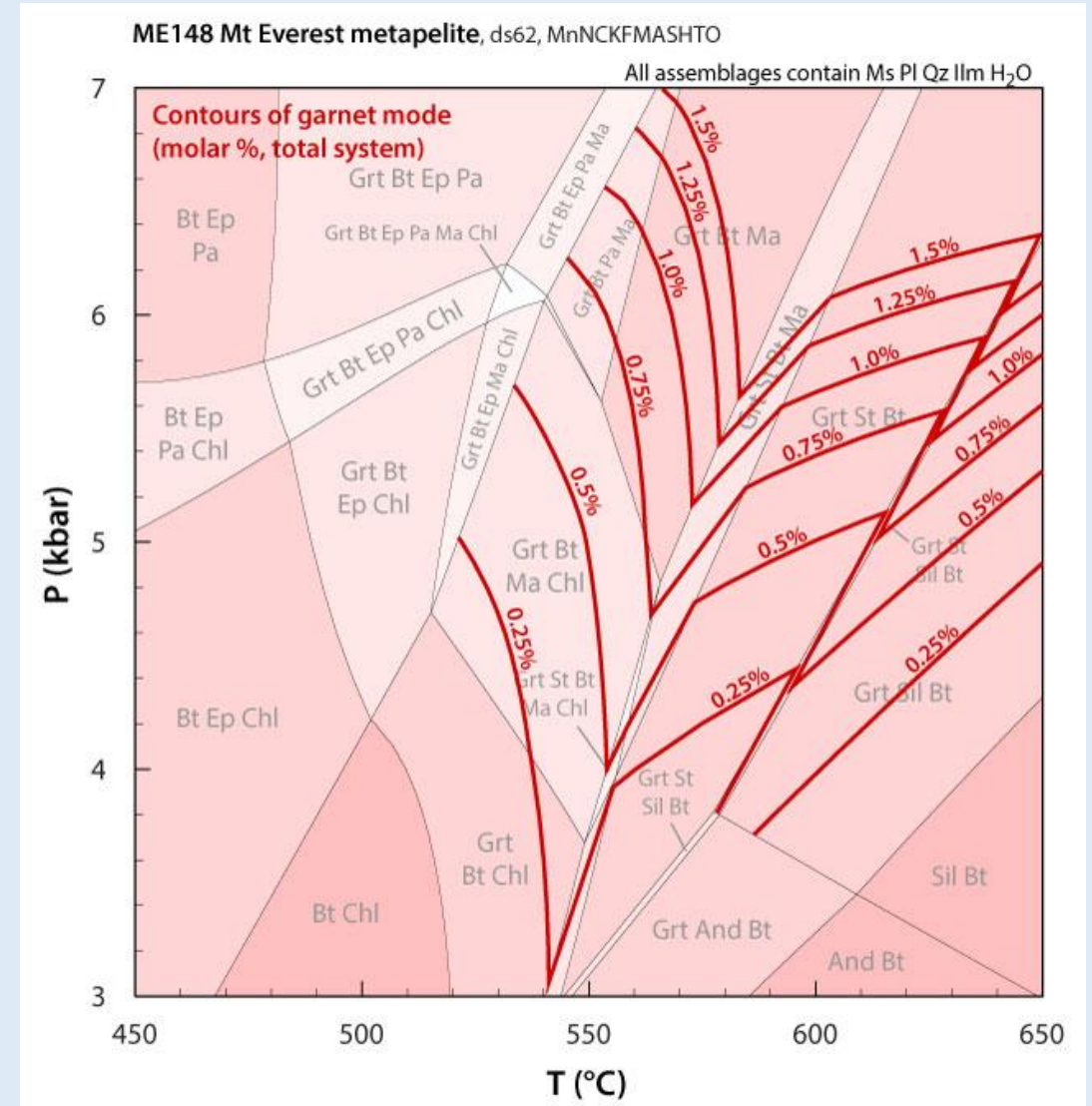
If the calculated assemblages include an H<sub>2</sub>O phase, either with moles H<sub>2</sub>O specified, or (prior to tc350) not specified but in excess, the mode of H<sub>2</sub>O is included in the total, but the results are, or can be (tc350), normalized to exclude the H<sub>2</sub>O mode.

When a mode contour is set, its value relates to the total system, not just the solid phases.

In such cases, the normalized result gives a mode value higher than the input one, by a factor that depends on the amount of free H<sub>2</sub>O.

Mode contours give a useful impression of the volume distribution across fields, but they are **not volume modes**, and **do not always correspond to input contour values**.

- See later for **TCInvestigator**, a partial solution



# Phase compositions and other parameters

- Determining full phase compositions – you can use ...
  - The 'xyz' parameters in the standard output contain this information, but not necessarily in a convenient form
  - The 'rbi' matrix contains molar information for bulk composition and all relevant phases, more easily converted into mineral formula units (cations)
- Other parameters:
  - Calculation method is not suited to determining all physical parameters of the rock
    - Densities of mineral phases are now (tc350) part of the output in the '-ic' file

## The RBI matrix (for metapelite ME148 at staurolite isograd, tc350 format)

rbi			H2O	SiO2	Al2O3	CaO	MgO	FeOt	K2O	Na2O	TiO2	MnO	O
rbi	g	0.008139	0	3.000000	0.979782	0.242451	0.308587	1.944387	0	0	0	0.545011	0.020218
rbi	pl	0.192818	0	2.599991	0.700004	0.400009	0	0	0.001812	0.298183	0	0	0
rbi	ma	0.093446	1	2.297133	1.839747	0.720493	0.009947	0.013426	0.015678	0.124075	0	0	0.002873
rbi	mu	0.201978	1	3.002556	1.483884	0.021971	0.013841	0.015834	0.344657	0.144357	0	0	0.002574
rbi	bi	0.208071	0.928735	2.649310	0.788695	0	1.153298	1.538005	0.500000	0	0.071265	0.010731	0.061995
rbi	st	0	2	7.500000	8.876082	0	0.750352	3.294475	0	0	0.080463	0.095725	0.070276
rbi	chl	0	4	2.499688	1.418400	0	2.484688	2.155444	0	0	0	0.023381	0.081912
rbi	ilmm	0.007116	0	0	0	0	0.020844	1.040508	0	0	0.903662	0.034986	0.096338
rbi	q	0.165495	0	1	0	0	0	0	0	0	0	0	0
rbi	H2O	0.122937	1	0	0	0	0	0	0	0	0	0	0
-----													
%													
% bulk			20.0002	49.8595	12.7561	2.9580	3.5410	5.3611	2.5580	1.9920	0.6150	0.1170	0.2420



# Extended output from tc350 – the ‘-ic’ file

New for tc350: Full data summary for each calculation

In a series of data blocks, lists:

- Values for ‘xyz’ phase composition variables
- Site fractions for elements in each phase
- Compositions in oxide units for the bulk and each phase, plus the molar ‘mode’ of each phase (not normalized for H<sub>2</sub>O)
- Thermodynamic quantities (G, H, S, V) and density for each phase, and for the bulk system
- Activity details for each end member in each phase, including standard state chemical potential ( $\mu_0$ ) and  $RT \ln a$  value

Roughly equivalent to Theriak’s ‘Thkout’ output file, and to Perple\_X output

Excerpts (for Grt and Pl) from tabulated results in ‘-ic’ file for metapelite ME148 at c. 4.8 kbar on staurolite isograd

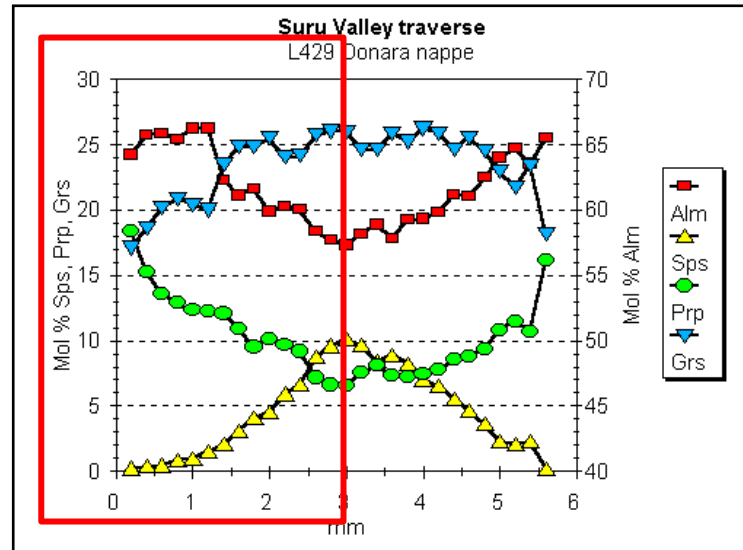
g	x(g)	z(g)	m(g)	f(g)			
	0.86053	0.08082	0.18167	0.02022			
pl	ca(pl)	k(pl)					
	0.40001	0.00362					
site fractions							
g	xMgX	xFeX	xMnX	xCaX	xAlY	xFe3Y	
	0.10286	0.63465	0.18167	0.08082	0.97978	0.02022	
pl	x(K)	x(Na)	x(Ca)				
	0.00362	0.59637	0.40001				
[RBI matrix (omitted)]							
[Thermo data]							
	G	H	S	V	rho		
g	-5910.5622	-5243.1922	0.7956	11.77755	4.11683		
pl	-4261.5988	-3847.8821	0.4932	10.14700	2.64772		
sys	-881.60009	-782.88781	0.11768	2.24290	2.57523		
	ideal	gamma	activity	prop	μ0	RT ln a	
g	py	0.00104479	1.75248	0.00183097	0.082644	-6581.3188	-43.9599
	alm	0.245393	1.04533	0.256517	0.63465	-5625.5352	-9.4893
	spss	0.00575586	1.10111	0.00633781	0.18167	-6049.2824	-35.2997
	gr	0.000506721	1.76420	0.000893959	0.080817	-6925.6331	-48.9603
	kho	4.44885e-7	8.59033	3.82171e-6	0.020218	-5734.3620	-87.0061
pl	abh	0.596367	1.09059	0.650391	0.59637	-4141.1122	-3.0003
	anC	0.400009	1.14534	0.458145	0.40001	-4431.9860	-5.4441
	san	0.00362463	71.0053	0.257368	0.0036246	-4177.8837	-9.4662





# Fractionation calculations

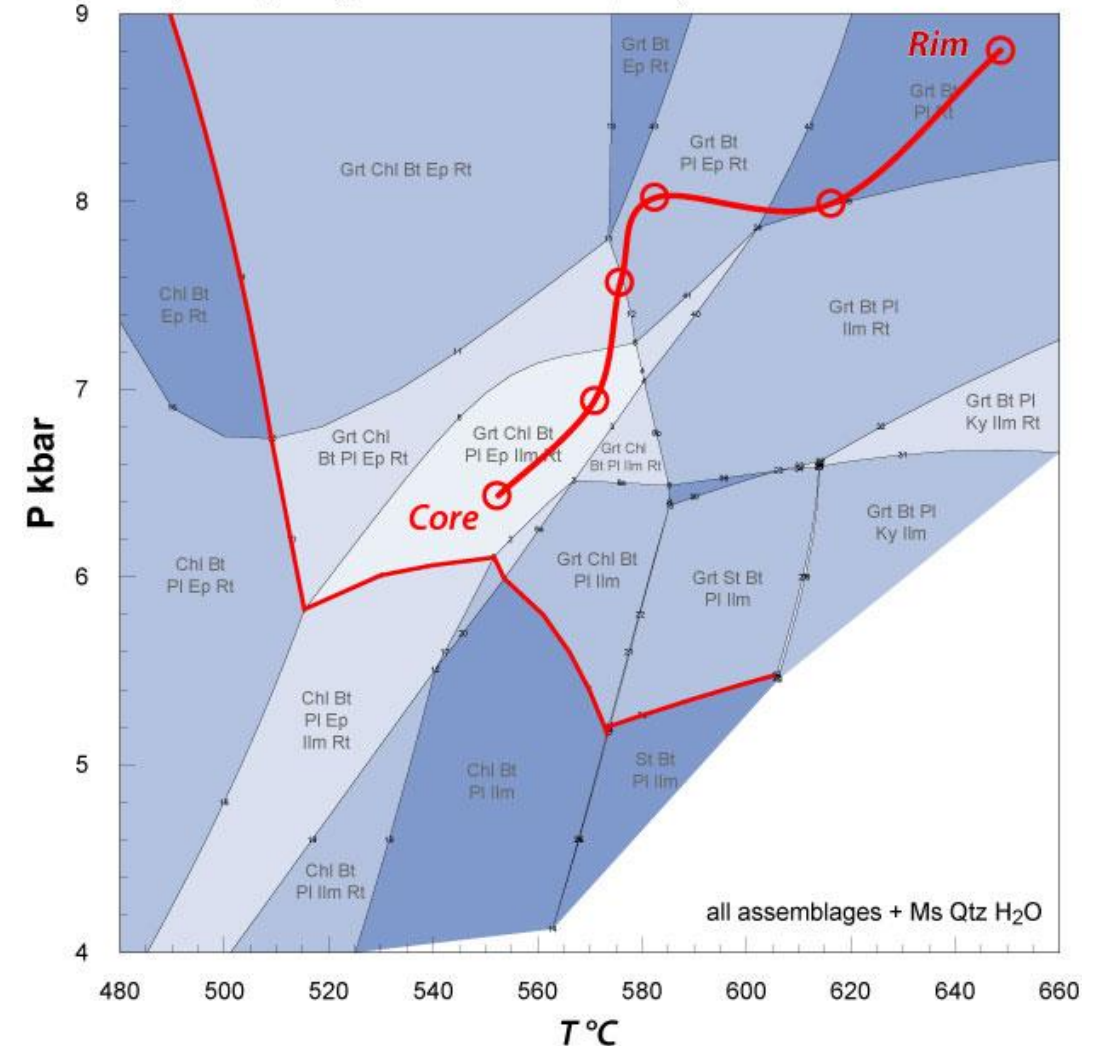
- Not wholly straightforward:
  - Requires stepwise manual adjustment of bulk composition guided by 'rbi' output of previous run
  - Watch out for changes in mineral assemblage
- Example: ***P-T* path from zoned garnet**, shows five fractionation steps based on intersections of pyrope & grossular isopleths, superimposed on *P-T* phase diagram for the total bulk composition
- More functionality promised in the longer term (see website)



**L429 Donara metapelite, Zanskar Himalaya**

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	FeO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	O
70.94	10.20	1.05	6.62	5.89	3.72	0.51	0.94	0.06	0.07

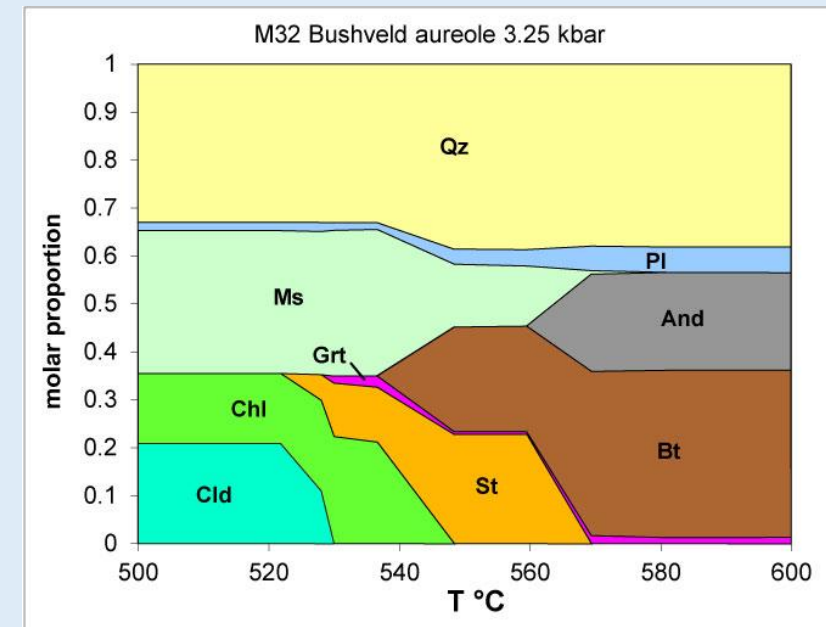
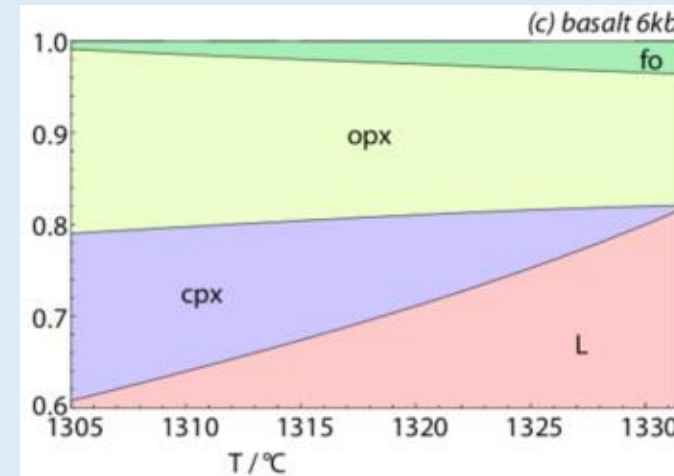
drawpd 1.15 (running at 13.20 on Sat 21 Nov, 2009)





# The 'modebox': plotting phase proportions

- Mode data always generated in 'pseudosection' calculations
- TC350 has a new script for organizing the data
- Needs auxiliary program to plot  
[some THERMOCALC output is designed to be readable by Mathematica®]
- Can do this manually, collect results, make preliminary plot in a spreadsheet program (e.g. MS-Excel), convert to filled chart in a graphics app.

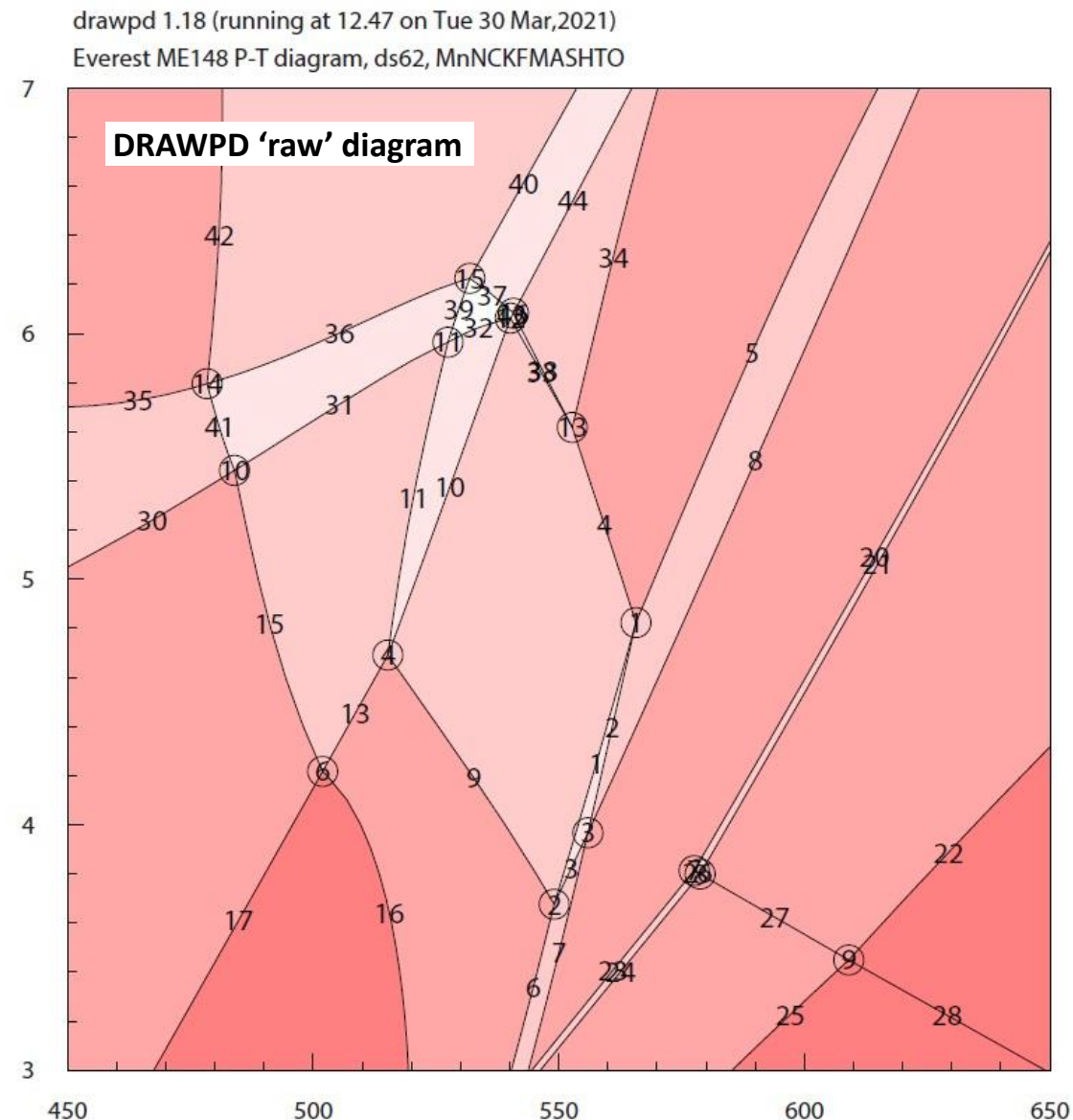


# Output: DRAWPD

- Supplementary program DRAWPD (draw.exe or dr11x.exe) takes output from THERMOCALC (-dr) file

Link: <https://hp xeosandthermocalc.org/downloads/download-drawpd-software/>

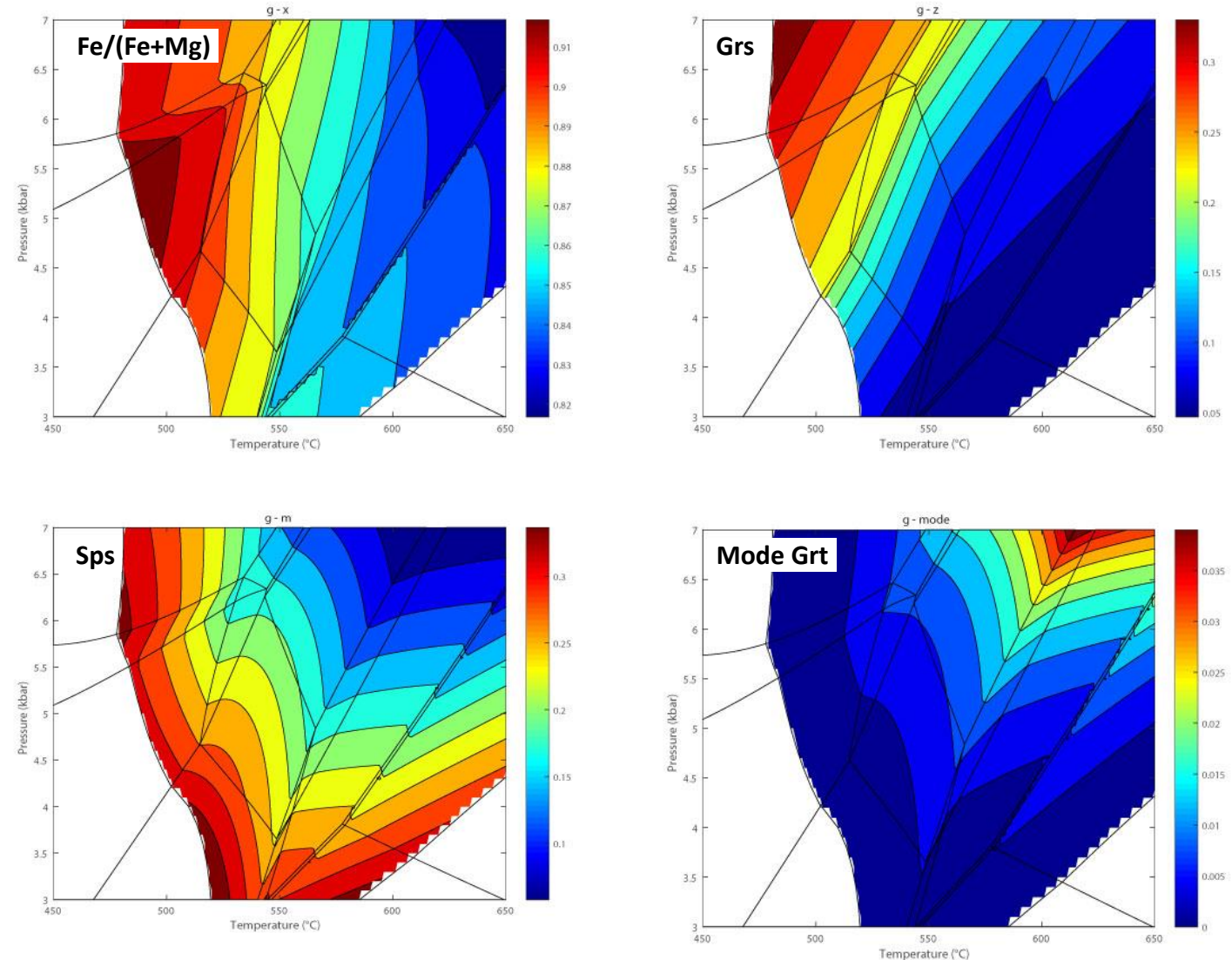
- Template dr-file is provided
- Input data requires some editing
- DRAWPD features:
  - Can define assemblage fields, recommends colouring according to variance
  - Optional: title, numbering of points and curves
  - Does not label axes
- Output as .eps file, editable in a vector graphics program, add axis labels etc., customize



# Other auxiliary programs

- **AX** – software by Tim Holland
  - Calculates activities for end members from primary analytical data, for use in **average *P-T*** calculations
  - Uses, or approximates, the then-current solution models
  - With TC v.3.50, users encouraged to use the HPx-eos rather than AX
- **TCInvestigator**
  - By Mark Pearce & others (CSIRO, Australia)
  - Use with TC v.3.4
  - Contours a completed phase diagram (pseudosection) for all parameters
  - Grids the actual (normalized) output results (i.e., avoids the “H<sub>2</sub>O effect” for modes)

TCInvestigator plots for Grt in Mt Everest metapelite ME148

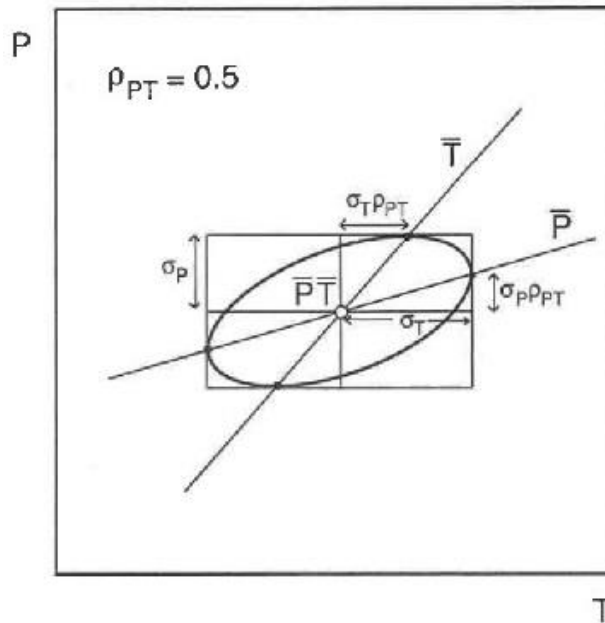
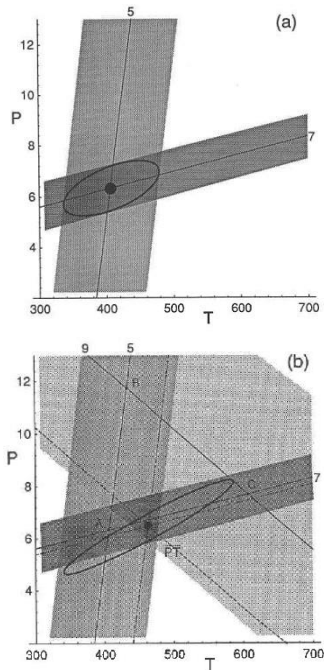
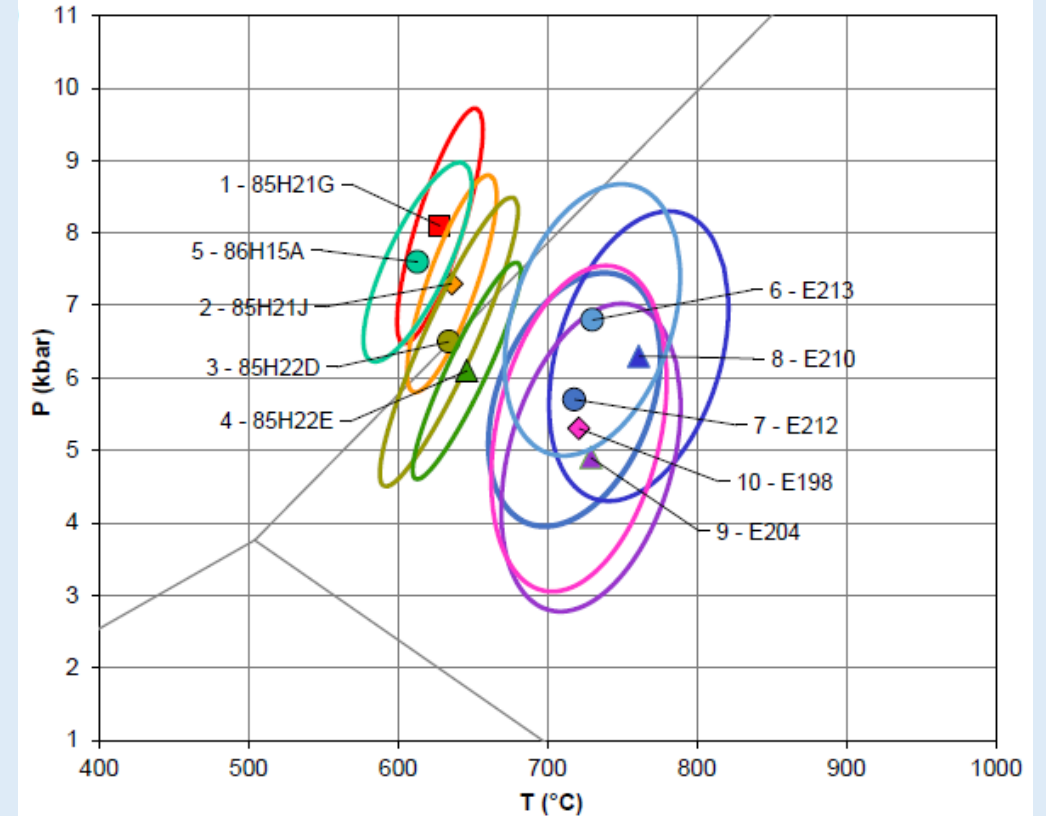


# Mode 2: Thermobarometry – “average $P$ - $T$ ”

- **Average  $P$ - $T$** , the inverse approach, was the primary purpose and major application of THERMOCALC up to later 1990s
- Principles: optimal geothermobarometry (Powell & Holland 1994)
  - Use all compositional information in the assemblage
  - Find independent set of equilibria among end members
  - Find weighted best-fit  $P$ - $T$  result with uncertainty ellipse

Example: Himalayan  $P$ - $T$  conditions south of Mt Everest, across the ‘inverted metamorphic sequence’

(data from Searle et al. 2003, figure from Waters 2019)





# Average *P* example (1) - getting started

This is THERMOCALC in **mode 2**

- Setting up the problem:  
Average *P*, average *T*, or average *P-T*?
- Selection of end member activities:  
(1) use AX (or another external  $\alpha$ -X model), or  
(2) use HPx-eos (coded solution models matched to HP dataset)
- Running the program: 3 input files ...
  - 'tc-prefs' file pointing to the script and dataset files
  - Script file containing name of the axfile, plus other scripts. If using method (2), supply 'xyz' composition variables for solid solution minerals
  - 'axfile' with either (method 1) activities of all relevant mineral end members, or (method 2) solution models for the activity calculations

Using tc350 with the coded solution models:-

Mt Everest garnet-zone metapelite L8 (Jessup et al. 2008)

'xyz' variables converted to activities: garnet example

variable	value	endmem	activity	sd(a)
x(g)	0.866	alm	0.5249	0.0343
		py	0.0033	0.0020
z(g)	0.064	gr	0.0008	0.0012

## Independent set of reactions

- 1)  $\mu + 2\text{phl} + 6\text{q} = \text{py} + 3\text{cel}$
- 2)  $2\text{east} + 6\text{q} = \text{py} + \mu + \text{cel}$
- 3)  $\mu + 2\text{annm} + 6\text{q} = \text{alm} + 3\text{fcel}$
- 4)  $3\text{anC} + \text{phl} = \text{py} + \text{gr} + \mu$
- 5)  $3\text{anC} + \text{annm} = \text{alm} + \text{gr} + \mu$
- 6)  $3\text{fcel} + 4\text{pa} = \text{alm} + 4\text{abh} + 3\mu + 4\text{H}_2\text{O}$

## Results (average *P*)

TjC	450	475	500	525	550	575	600	625	650
av P	5.26	5.46	5.65	5.83	6.01	6.18	6.34	6.49	6.62
sd	1.59	1.50	1.44	1.38	1.35	1.34	1.34	1.37	1.41
sigfit	2.07	1.96	1.87	1.80	1.75	1.74	1.75	1.78	1.85

Independent T estimate (Grt-Bt, Ti-in-Bt) is 560 – 580°C



# Average P example (2) - diagnostics

Diagnostics (doubling uncertainty on activity) for first run with Everest metapelite L8

	P	sd	sigfit	e*	hat	a(obs)	a(calc)	e*	hat	
py	6.00	2.09	3.396	0.582	0.011	0.00335	0.00484	0.323	0.000	
alm	5.92	2.05	3.334	-0.937	0.001	0.524	0.492	-1.000	0.002	
gr	6.14	2.20	3.386	0.849	0.149	0.000877	0.00331	-0.023	0.000	
abh	6.27	2.08	3.297	-1.209	0.027	0.619	0.577	-0.390	0.006	
anC	5.98	2.09	3.403	-0.114	0.003	0.478	0.475	0.198	0.001	
mu	5.97	2.09	3.404	0.059	0.000	0.754	0.755	0.149	0.000	
cel	5.85	2.35	3.400	-0.348	0.253	0.0159	0.0146	0.090	0.011	
fcel	4.92	1.84	2.790	-4.349	0.153	0.0303	0.0105	-1.023	0.004	
pa	6.91	2.05	3.050	3.037	0.168	0.631	0.980	0.439	0.007	
phl	6.15	2.02	3.269	2.056	0.017	0.0848	0.167	-0.049	0.000	
anm	5.34	1.73	2.753	3.666	0.036	0.0721	0.142	1.362	0.005	
east	6.55	2.16	3.250	-1.867	0.117	0.109	0.0771	-0.534	0.014	
q	5.97	2.09	3.404	0	0	1.00	1.00	0.636	0.015	
H2O	5.97	2.09	3.404	0	0	1.00	1.00	-0.053	0.000	
TjC		450	475	500	525	550	575	600	625	650
av P		3.55	4.23	4.85	5.43	5.97	6.47	6.93	7.35	7.73
sd		2.885	2.684	2.479	2.277	2.085	1.910	1.761	1.645	1.570
sigfit		5.016	4.576	4.157	3.764	3.404	3.085	2.817	2.612	2.483

## Interpreting and refining results

- Poor result? Consider excluding end members
- Look for large misfit  $e^* > 2.5$
- Relatively large 'hat' value = influential end member. Maybe good, but bad if  $e^*$  also large
- Look at effect on P, sd and sigfit of relaxing activity constraint: big shift to smaller sd and fit marks candidate for deletion
- Stop deleting when sigfit reaches acceptable value

*Rather large s.d.  
V. poor fit – should be <1.5*





# Average *P-T* examples (3)

Plotting and interpreting results for a subsolidus Alpine kyanite schist ...

% DW-034 Polinik Schist (calc at 620°C, 7 kbar)

% Garnet rim

py 0.0074 gr 0.000008 alm 0.50

% Mean biotite

phl 0.047 ann 0.055 east 0.042

% Mean muscovite

mu 0.70 pa 0.470

% Mean staurolite

mst 0.00092 fst 0.47

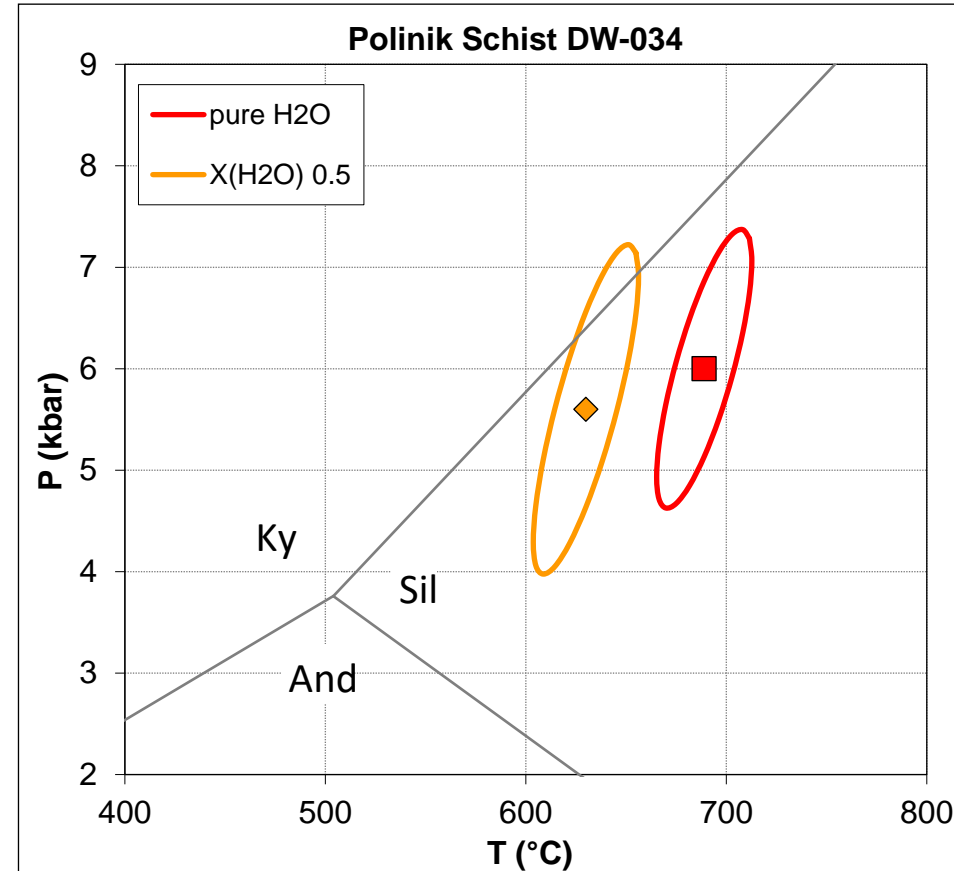
% Mean plagioclase

an 0.158 ab 0.90

ky q H<sub>2</sub>O

## Independent set of reactions

- 1)  $gr + 2ky + q = 3an$
- 2)  $6mst + 75an = 8py + 25gr + 96ky + 12H_2O$
- 3)  $6fst + 75an = 25gr + 8alm + 96ky + 12H_2O$
- 4)  $pa + 3an = gr + ab + 3ky + H_2O$
- 5)  $3east + 6q = py + phl + 2mu$
- 6)  $py + 3east + 4q = 3phl + 4ky$
- 7)  $ann + 2ky + q = alm + mu$



However, the results do not lie in the kyanite field, and the H<sub>2</sub>O-saturated result lies above the wet solidus.

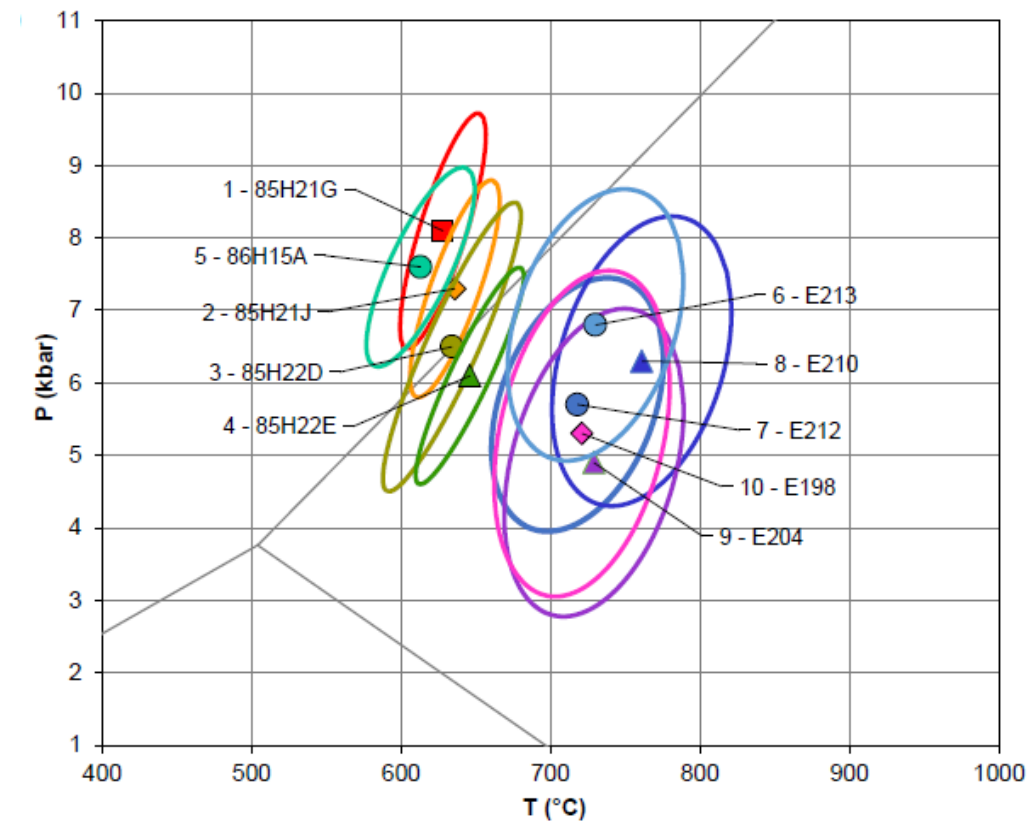
Consistency with calculated phase diagram is not guaranteed!

# Average $P$ - $T$ examples (4)

- **Average  $P$ - $T$  example, Mt Everest region, Himalaya**

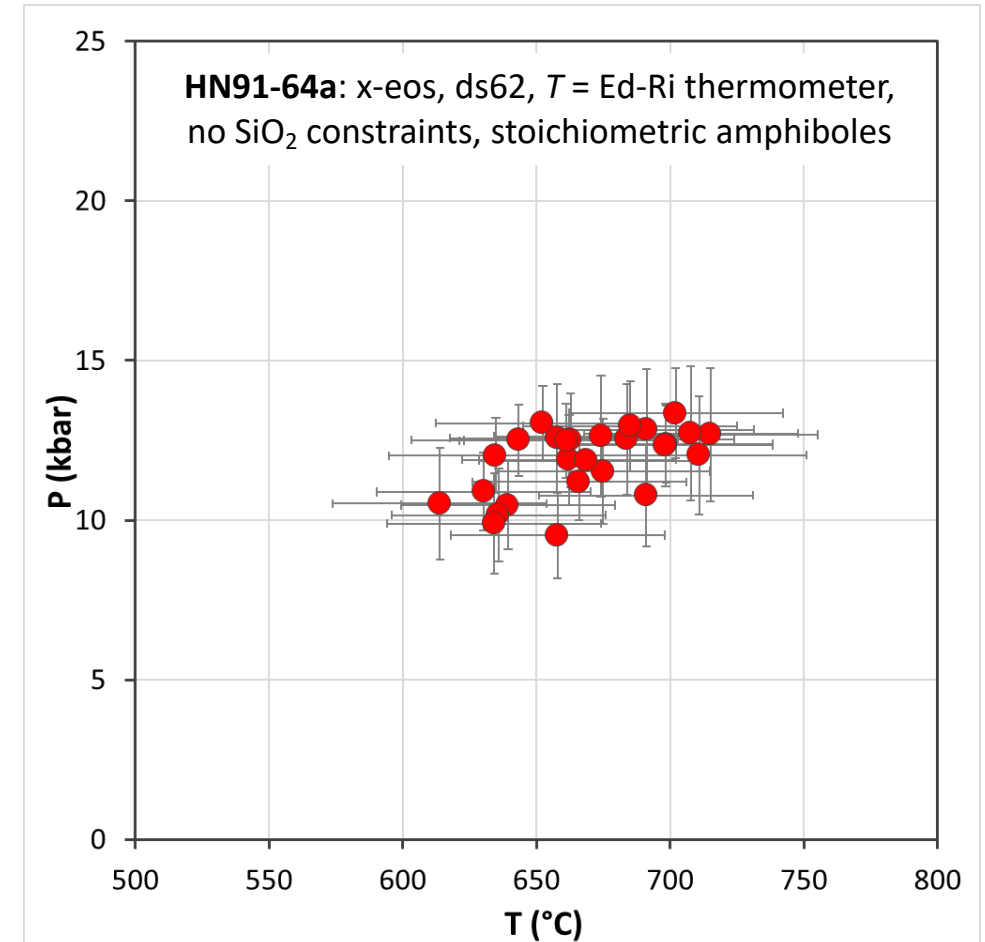
Two groups of samples with different assemblages:

- 1–5, muscovite-bearing upper amphibolite facies rocks
- 6–10, migmatitic Sil-Kfs zone gneisses, lacking muscovite



- **Average  $P$ , with independent  $T$  calculation**

- Western Gneiss Complex, Norway;  $P$ - $T$  array from local equilibrium in Cpx-Pl-Hbl symplectite after omphacite



# Mode 3: Calculate all reactions

- More useful than it might seem! Use pure end members, or with adjusted activities (based on a given sample)
- With Schreinemakers analysis: for  $P$ - $T$  projections (petrogenetic grids), see <https://hpxeosandthermocalc.org/the-thermocalc-software/thermocalc-calculation-facilities/thermocalc/extracting-dataset-information/>
- Without Schreinemakers analysis: see all equilibria, with slopes and uncertainties. Useful for ...
  - Checking sensitivity of individual equilibria
    - Implications for which end members to retain or exclude in average  $P$ - $T$
  - Discovering new geobarometers! (small  $sd(P)$ , small  $dP/dT$ )
    - Garnet – clinopyroxene – phengite, for eclogites (Waters & Martin, 1993)
    - Amphibole equilibria, e.g., in high-variance assemblages, symplectites (Waters, 2003)

Partial results for an assemblage Hbl-Di-Pl-Qz

*Reaction list (first 5 reactions):*

- 1) **jd + q = abh**
- 2) tsm + 2di + 2q = tr + 2anC
- 3) 7tsm + 2cumm + 14hed + 14q = 7tr + 2grnm + 14anC
- 4) **2prgm + 6abh = tr + tsm + 8jd**
- 5) 2prgm + 3glm + 6anC = tr + 4tsm + 8jd

*Reaction thermo data:*

	a	sd(a)	b	c	ln_K	sd(ln_K)
1	12.959	0.23	-0.045632	1.70566	1.196	0.187
2	14.552	0.54	-0.061624	2.62940	4.542	1.082
3	-39.902	9.31	-0.354815	19.21593	45.887	25.759
4	-173.201	1.99	0.453135	-12.18784	-15.980	1.896
5	-108.095	2.92	0.343997	-9.13372	-12.577	4.629

*P(kbar) at T:*

	550.00	600.00	650.00	700.00	750.00	sdT	sdP
1	9.6247	10.6734	11.7197	12.7629	13.8026	41	0.85
2	2.0463	2.4314	2.7919	3.1350	3.4780	472	3.24
3	1.0366	0.9064	0.7410	0.5695	0.3926	+	10.41
4	7.4558	8.7539	10.0566	11.3637	12.6747	46	1.19
5	9.7943	11.0650	12.3640	13.6926	15.0522	149	3.90



# THERMOCALC summary 1: strong and weak points

## ▪ Strengths:

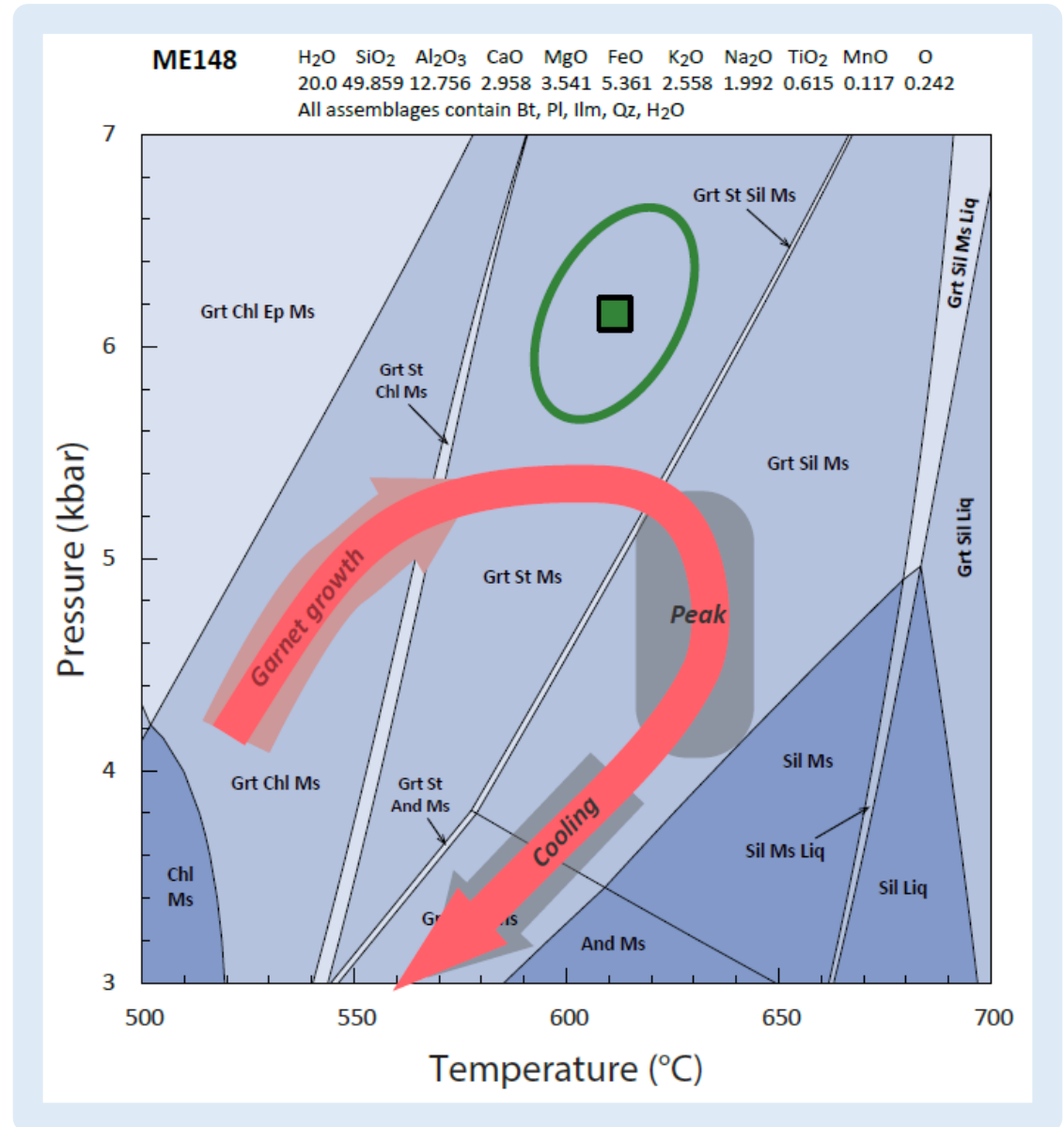
- Line-oriented, precise location of univariant curves and assemblage boundaries
- Learning opportunities about phase diagram properties from hands-on construction
- Forward and inverse modelling from the same package
- Assured consistency (we hope also accuracy!) from use of internally consistent datasets and HPx-eos solution models

## ▪ Disadvantages:

- More labour-intensive, steep learning curve, large time commitment for a complete diagram
- User must decide which mineral phases to include – significant opportunity for error
- *G*-minimization possible, but limited in scope, inefficient
- Tied to specific database and solution models (Holland & Powell dataset(s), and HPx-eos)
- Solution models are still ‘works in progress’ with known flaws (applies to all software that uses them)
- Some practitioners take issue with the way certain solution models are formulated
- Program crashes may occur, error messages could be more helpful, 1 or 2 elusive bugs.

# THERMOCALC summary 2: practical phase diagram strategies

- G-minimization: reconnaissance before starting
  - Using *dogmin* function in THERMOCALC?
  - Is quickest with another package (T/D, Perple\_X)
- Complete diagram in THERMOCALC,
  - For graphical precision of results
  - Variety of output information
  - For better understanding of phase relationships
- You then have an equilibrium phase diagram, which can be used for further (perhaps non-equilibrium) petrological interpretation ...



# Key references

- Holland, TJB, & Powell, R, 1998. An internally-consistent thermodynamic dataset for phases of petrological interest. *Journal of Metamorphic Geology* 16, 309-344.
- Pearce, MA, White, AJR, & Gazley, MF, 2015. TCInvestigator: Automated calculation of mineral mode and composition contours for THERMOCALC pseudosections. *Journal of Metamorphic Geology*, doi:10.1111/jmg.12126.
- Powell, R, & Holland, TJB, 1988 An internally consistent thermodynamic dataset with uncertainties and correlations: 3: application methods, worked examples and a computer program. *Journal of Metamorphic Geology* 6, 173-204.
- Powell, R, & Holland, TJB, 1994. Optimal geothermometry and geobarometry. *American Mineralogist* 79, 120-133.
- Powell, R, & Holland, TJB, 2008. On thermobarometry. *Journal of Metamorphic Geology*, 26, 155-179.
- Powell, R, Holland, TJB, & Worley, B, 1998. Calculating phase diagrams involving solid solutions via non-linear equations, with examples using THERMOCALC. *Journal of Metamorphic Geology* 16, 577-588.

