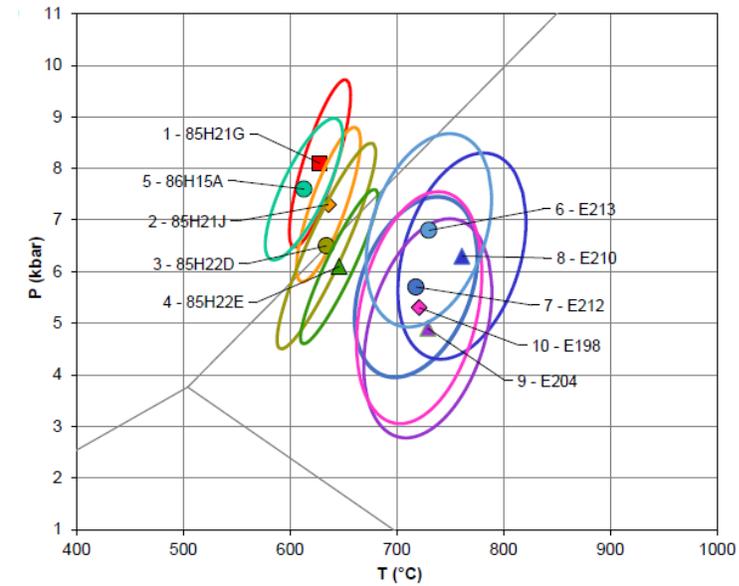


# THERMOCALC & average *P-T*

Dave Waters  
 University of Oxford, UK



# Introduction to THERMOCALC

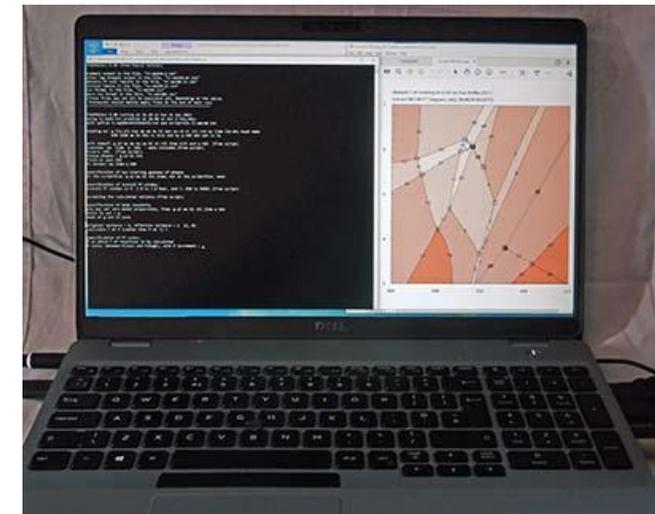
- Origins and landmarks ...
  - Roger Powell doctoral thesis 1973, suite of FORTRAN programs on University mainframe.
  - Holland & Powell 1985 – 1990: internally consistent thermodynamic datasets
  - THERMOCALC release 1988, calculating reactions, average  $P$ - $T$ , uncertainties
  - Pseudosections: 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)

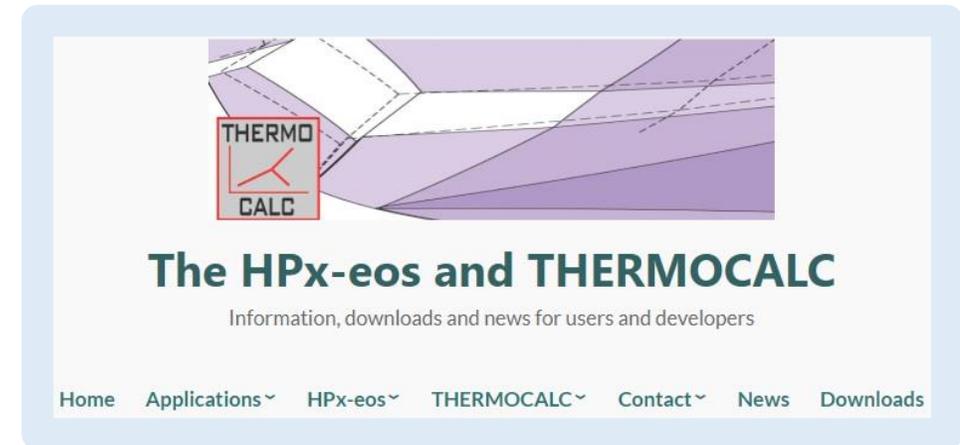
Useful links to older information and archived documents:

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

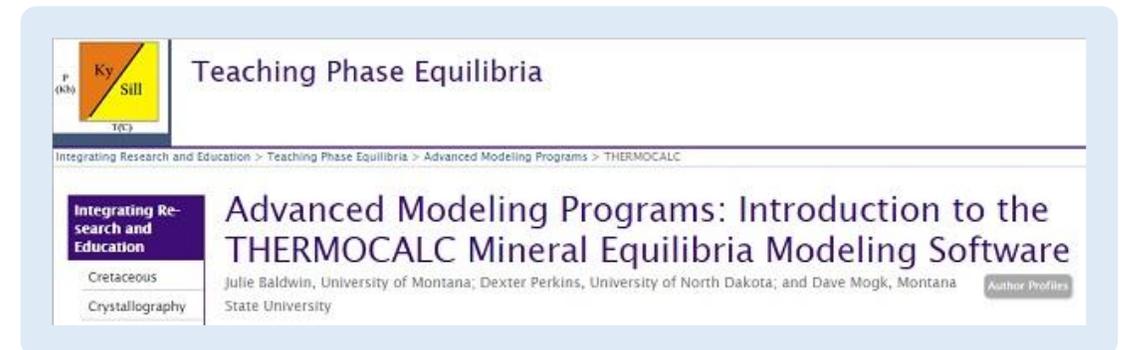
[https://serc.carleton.edu/research\\_education/equilibria/thermocalc.html](https://serc.carleton.edu/research_education/equilibria/thermocalc.html)

[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/>



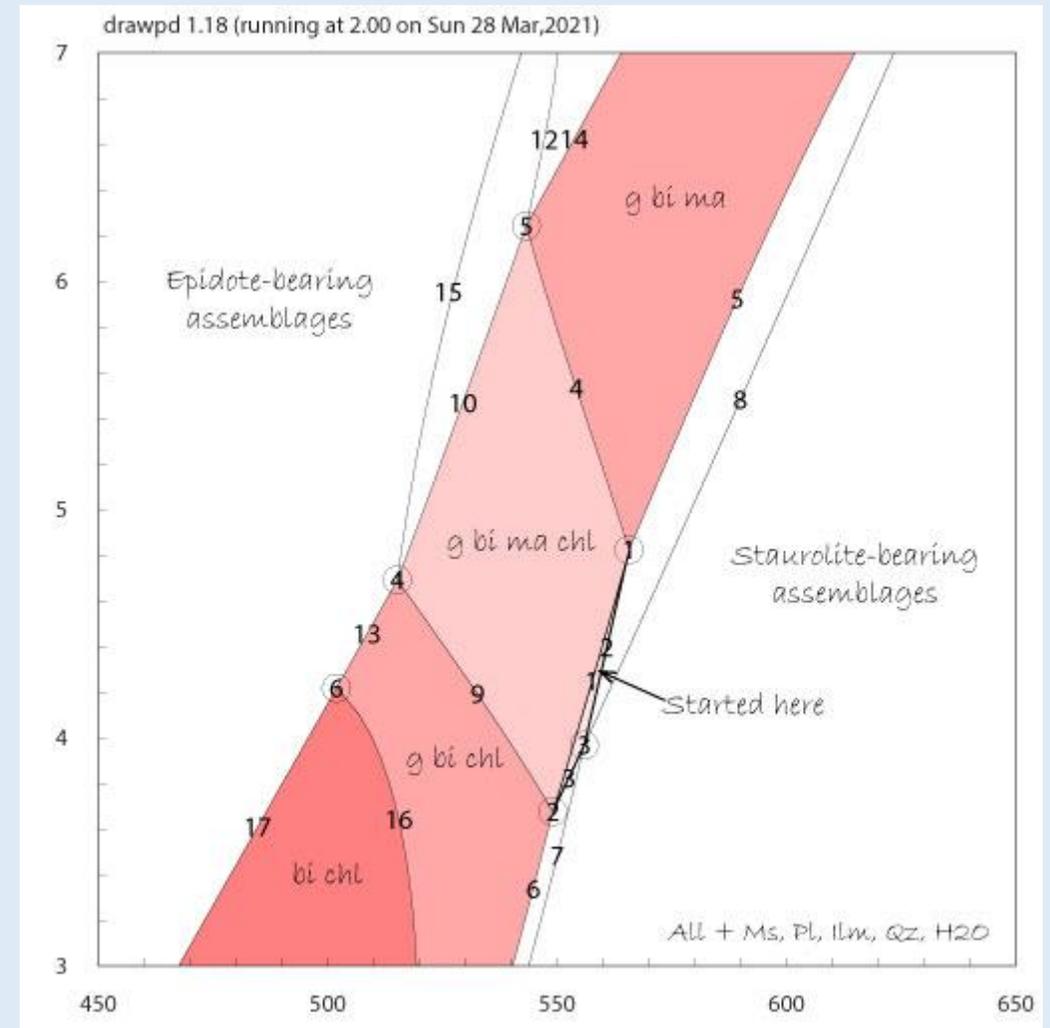
[https://serc.carleton.edu/research\\_education/equilibria/thermocalc.html](https://serc.carleton.edu/research_education/equilibria/thermocalc.html)



# 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 ...







# 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):

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

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

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

$$f(g) = x\text{Fe}^{3+}$$

Coding for proportion of pyrope in garnet:

|                |   |   |   |   |    |   |    |   |    |   |    |   |
|----------------|---|---|---|---|----|---|----|---|----|---|----|---|
| $p(\text{py})$ | 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:

|               |   |   |   |   |    |   |    |   |    |   |  |  |
|---------------|---|---|---|---|----|---|----|---|----|---|--|--|
| $x\text{MgX}$ | 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 | $x\text{MgX}$ | 3 | $x\text{AlY}$ | 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:

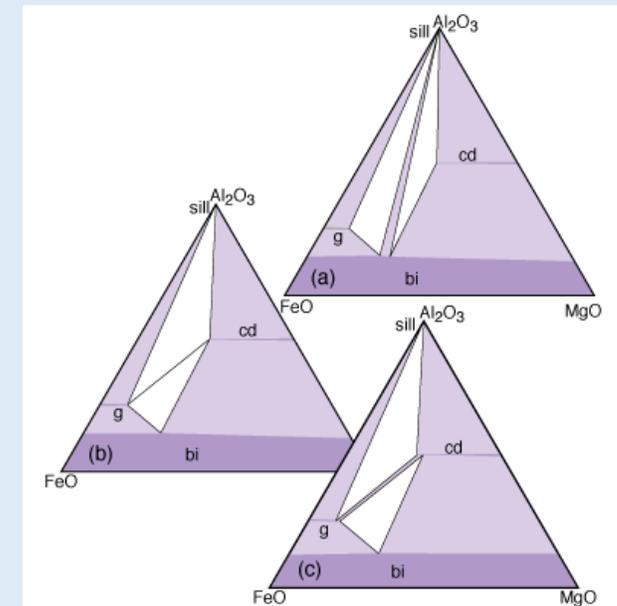
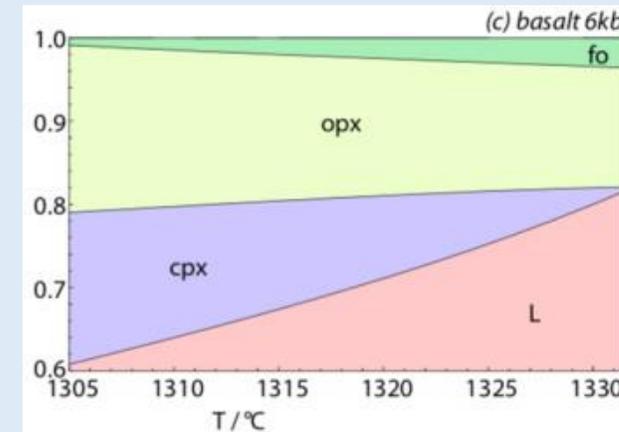
| Mode | g        | pl      | ma      | mu      | bi      | st      | ... |
|------|----------|---------|---------|---------|---------|---------|-----|
|      | 0.004553 | 0.2831  | -       | 0.2936  | 0.1693  | -       | ... |
| sd   | 0.00142  | 0.00127 | 0.00242 | 0.00385 | 0.00174 | 6.14e-5 | ...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



# 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



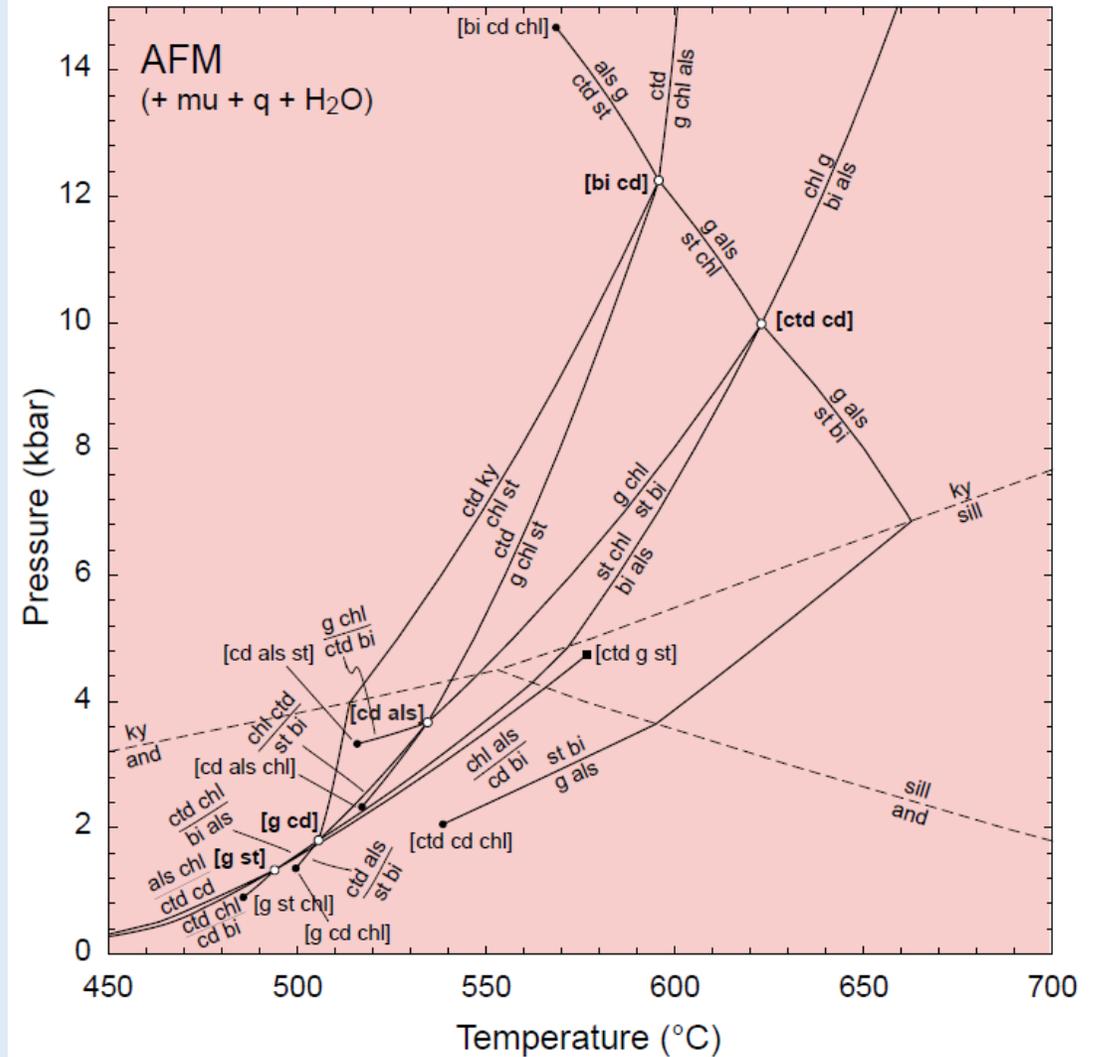
# P-T projection

- 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.

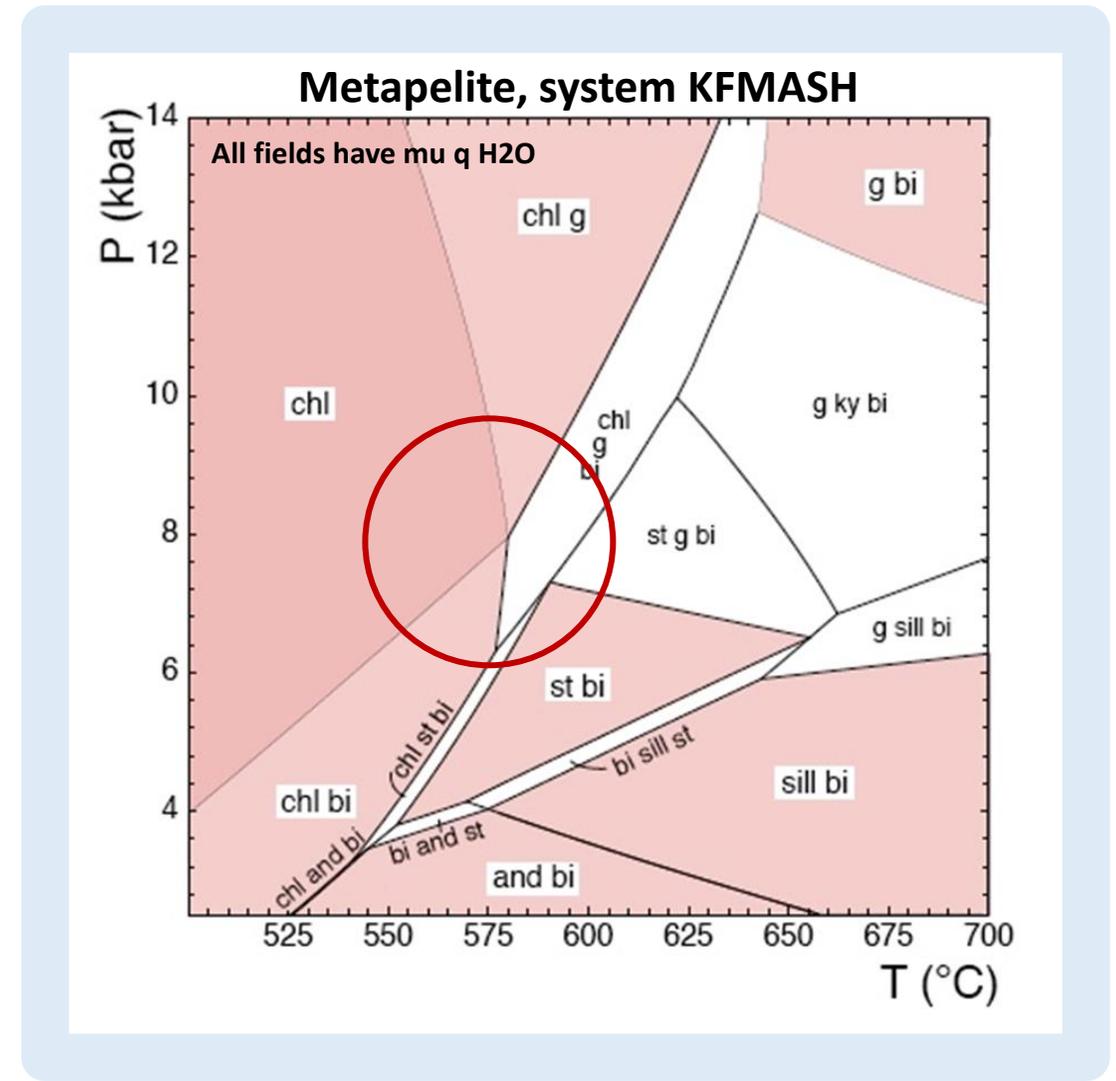
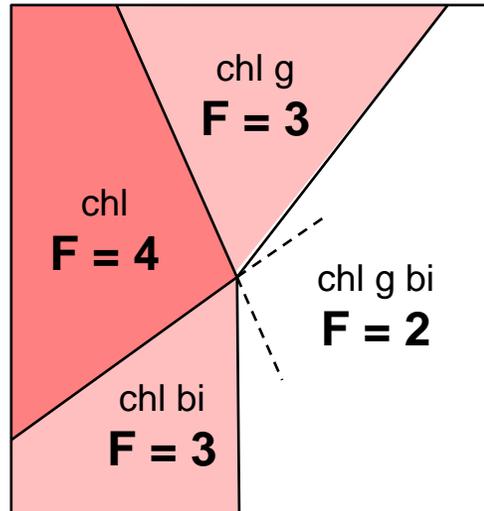
- Diagram consists of linked bundles of stable reaction curves arranged according to Schreinemakers' rules
- Note some curves terminate in simpler end-member systems

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!

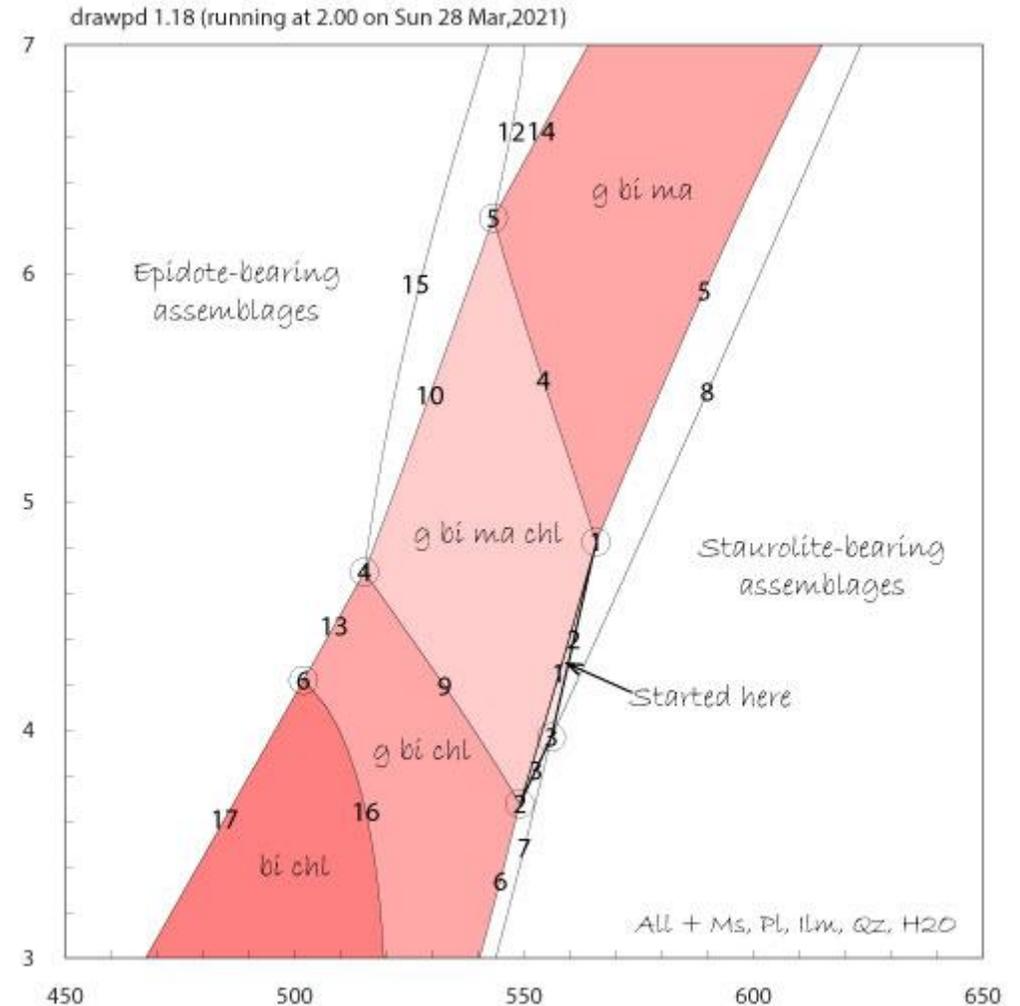
A promising area  
to start work? →

| 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):

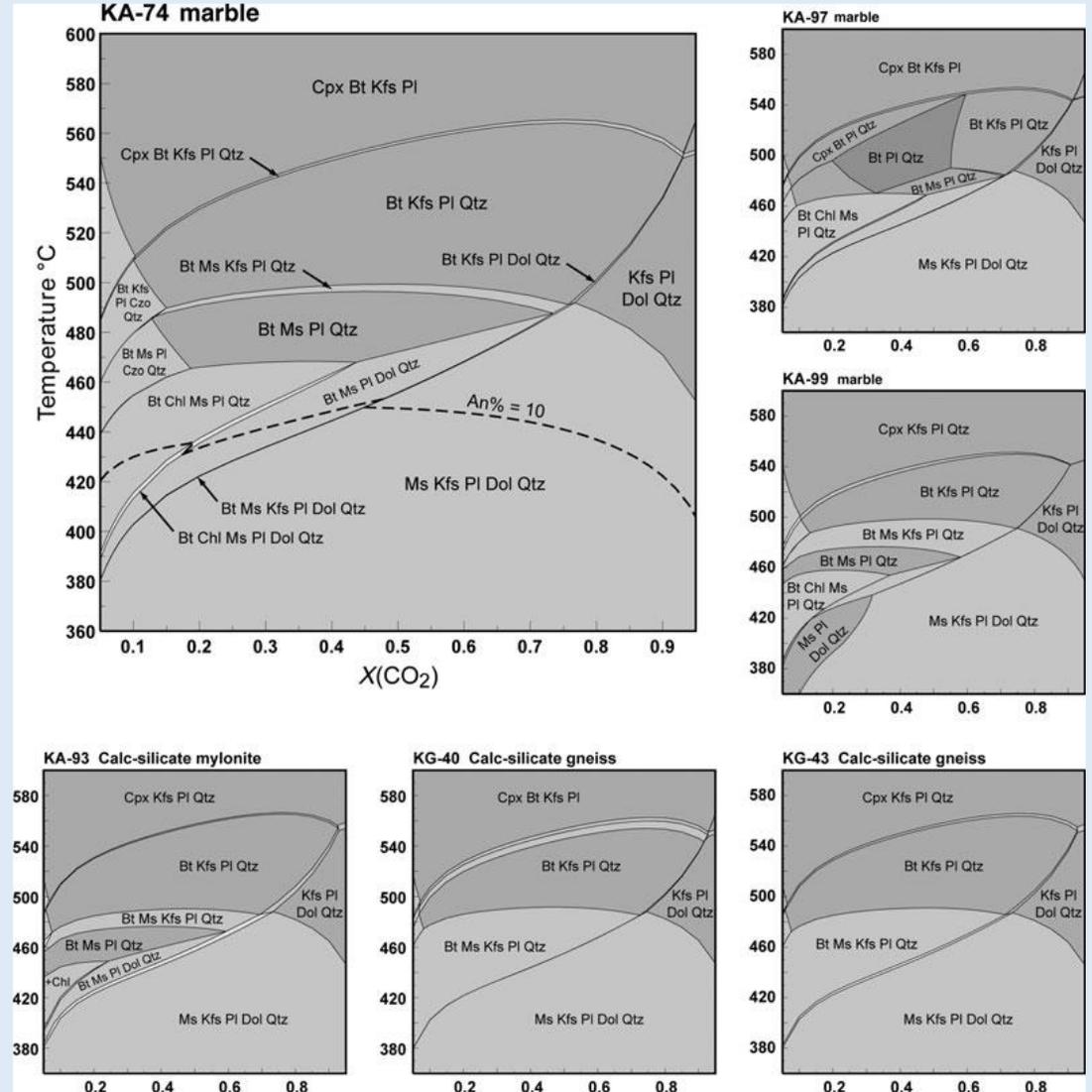
```
% at P = 4.8, T = 566, for: g pl ma mu bi st chl ilmm q ...
% -----
ptguess 4.823 565.70
% -----
xyzguess x(g)          0.860528
xyzguess z(g)          0.0808171
xyzguess m(g)          0.181670
xyzguess f(g)          0.0202180
% -----
xyzguess ca(pl)        0.400009
xyzguess k(pl)         0.00362463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



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

- Where X is fluid composition, e.g., H<sub>2</sub>O – CO<sub>2</sub>
    - Calculations performed at specified increments along the X axis
  - Other examples
    - T-X(Mg) see next slide
    - T-X(Fe<sup>3+</sup>) varying oxidation state of Fe
    - T-M(H<sub>2</sub>O) varying moles of H<sub>2</sub>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

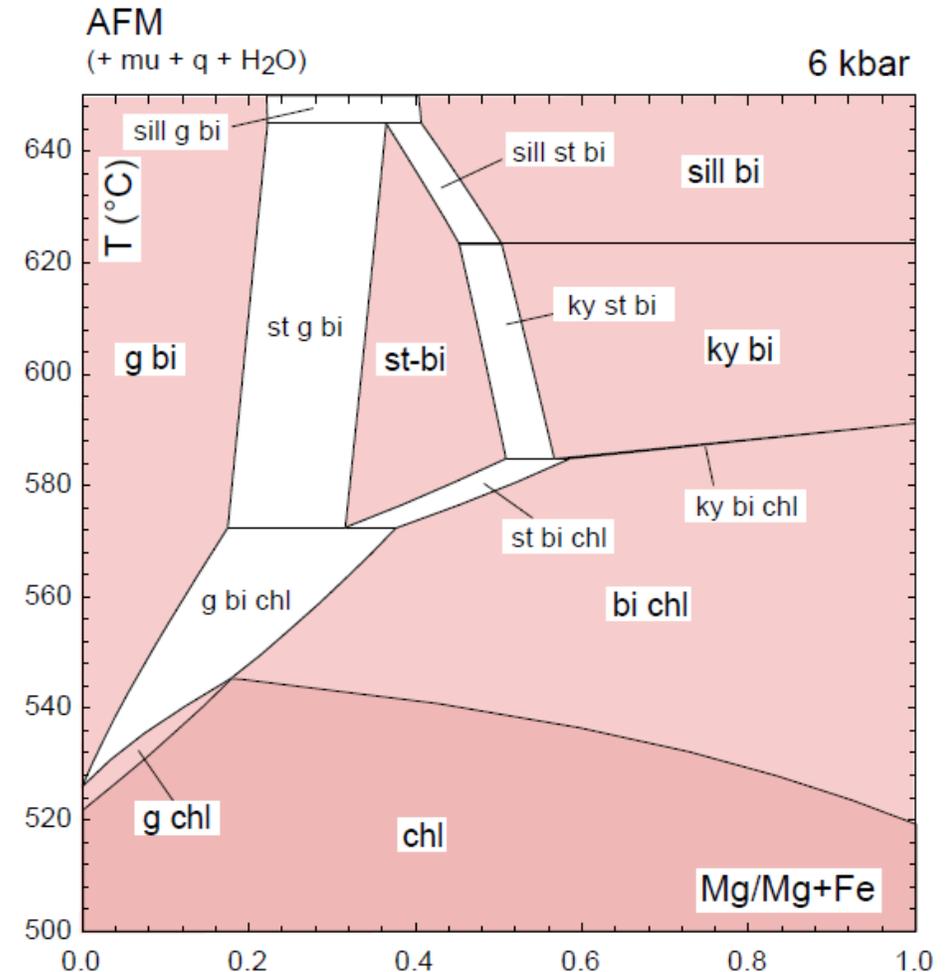


# T-X (or P-X) phase diagram (2)

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

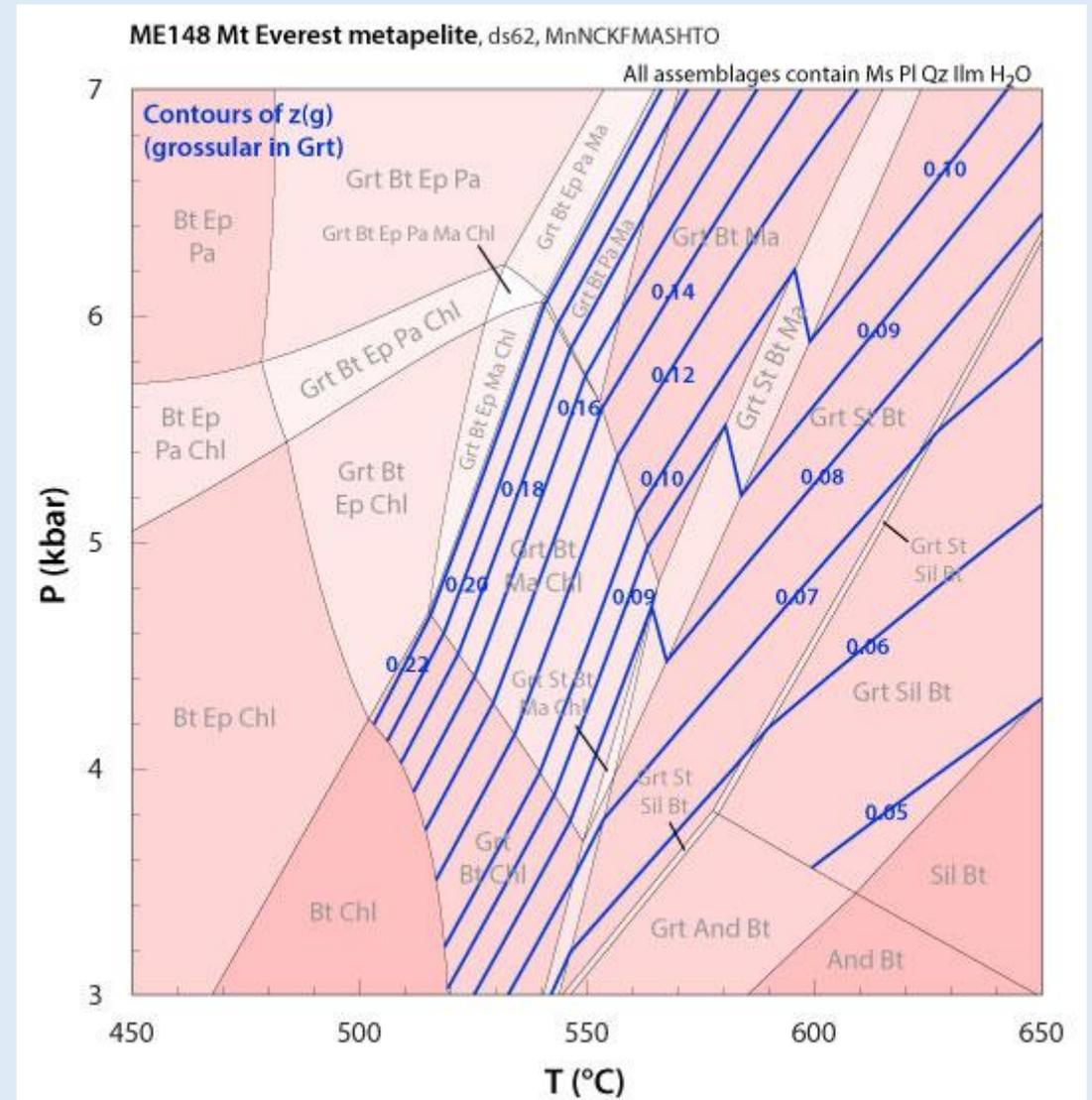
- Each isopleth is treated as a univariant curve
- Each assemblage field must be treated in turn

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  $f(\text{g})$



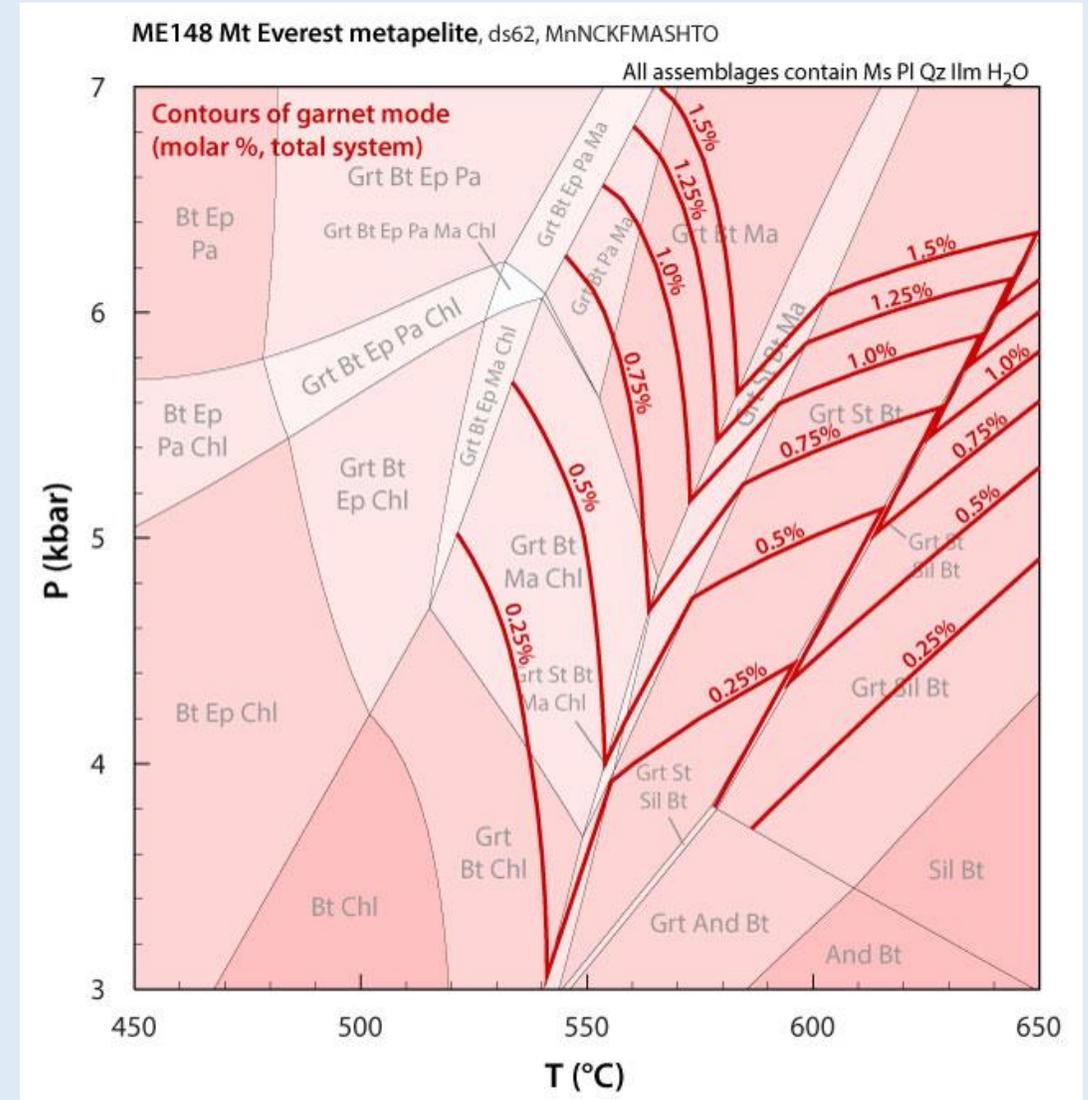
# Mode isopleth calculations

- 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

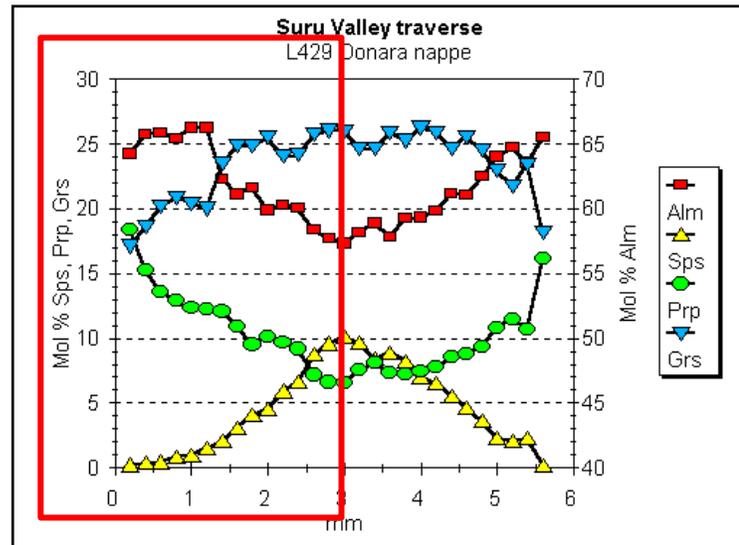
          ideal      gamma      activity      prop           $\mu_0$       RT ln a
g  py      0.00104479  1.75248  0.00183097  0.082644  -6581.3188  -43.9599
   alm     0.245393  1.04533  0.256517   0.63465  -5625.5352  -9.4893
   spss    0.00575586  1.10111  0.00633781  0.18167  -6049.2824  -35.2997
   gr      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

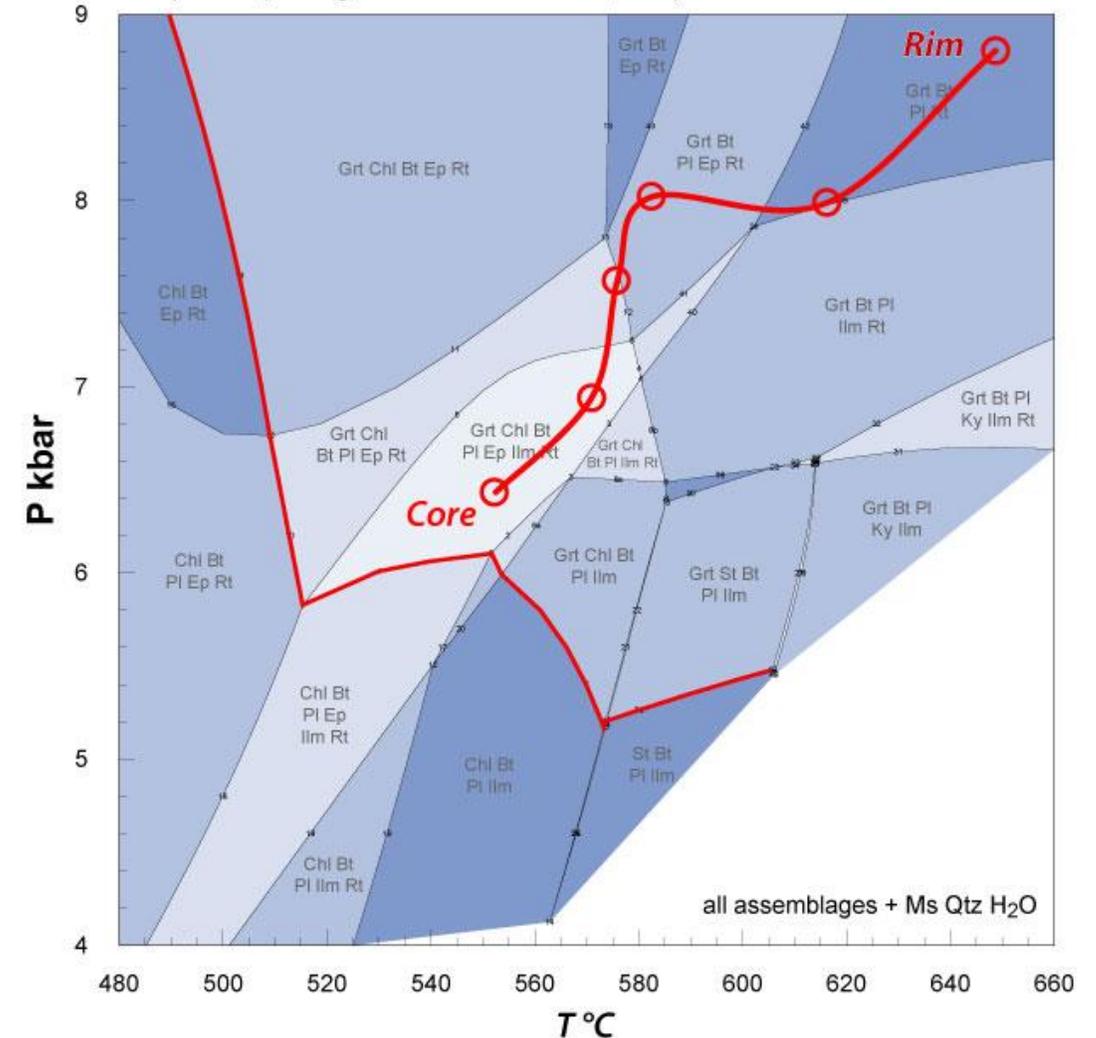
- Not wholly straightforward:
  - Requires stepwise manual adjustment of bulk composition guided by 'rbi' output of previous run
  - Watch out for changes in mineral assemblage
- Example: ***P-T* path from zoned garnet**, shows five fractionation steps based on intersections of pyrope & grossular isopleths, 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

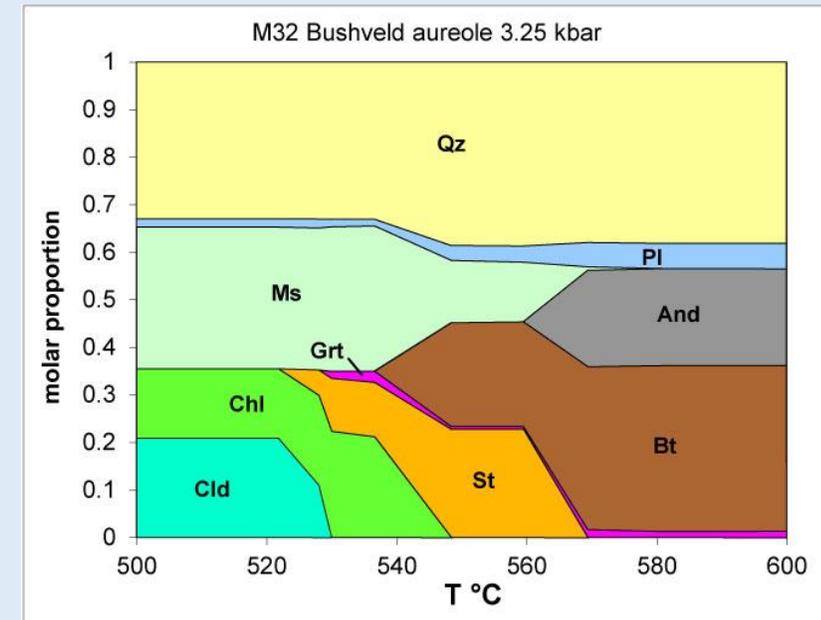
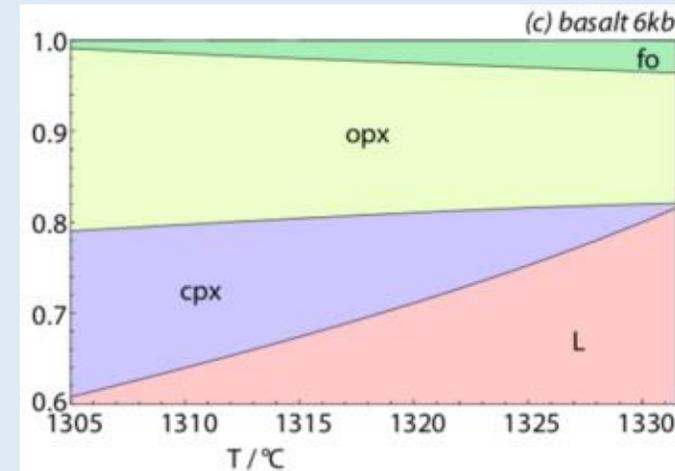
| SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | FeO  | K <sub>2</sub> O | Na <sub>2</sub> O | TiO <sub>2</sub> | MnO  | O    |
|------------------|--------------------------------|------|------|------|------------------|-------------------|------------------|------|------|
| 70.94            | 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.

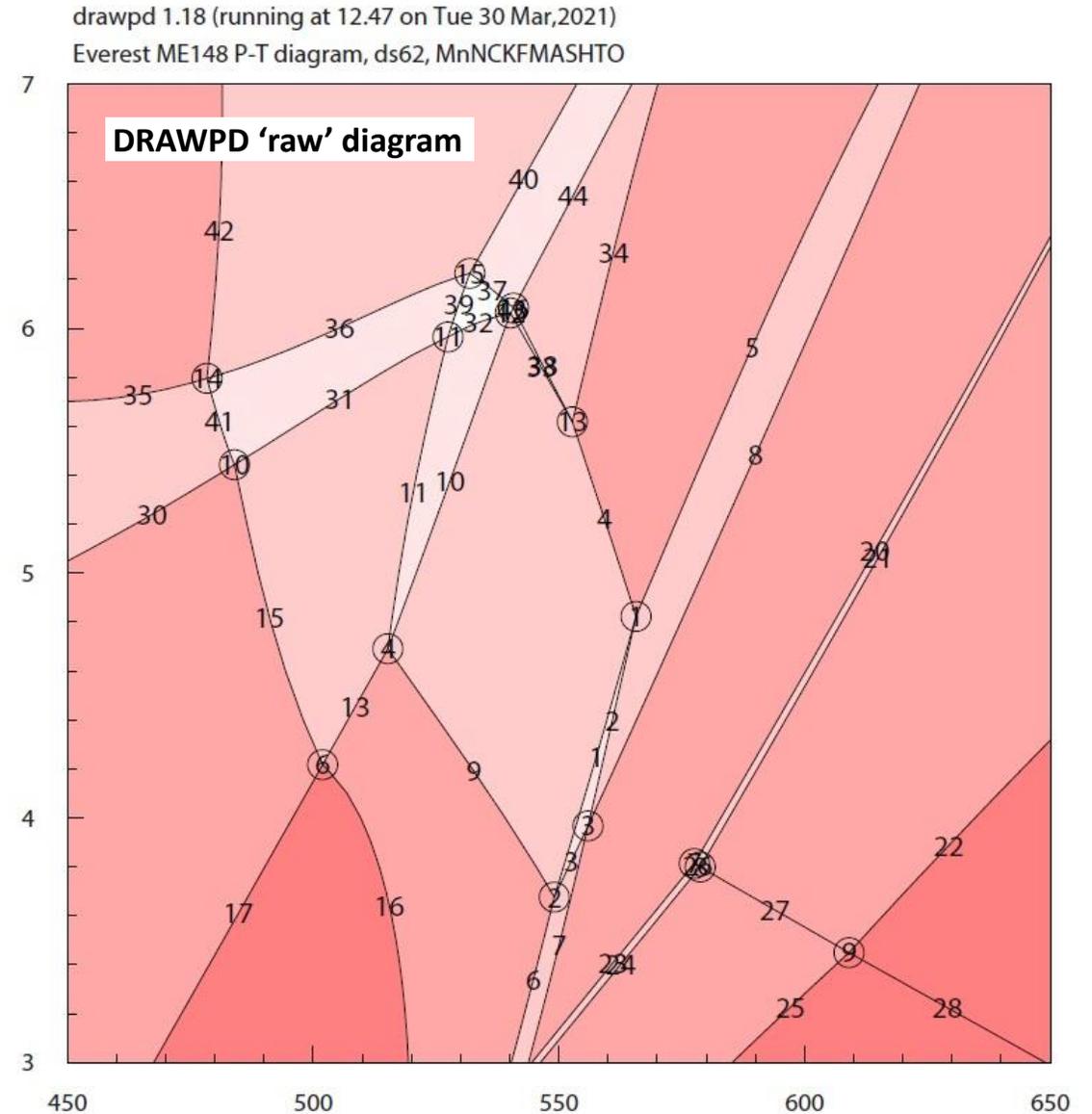


# Output: DRAWPD

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

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

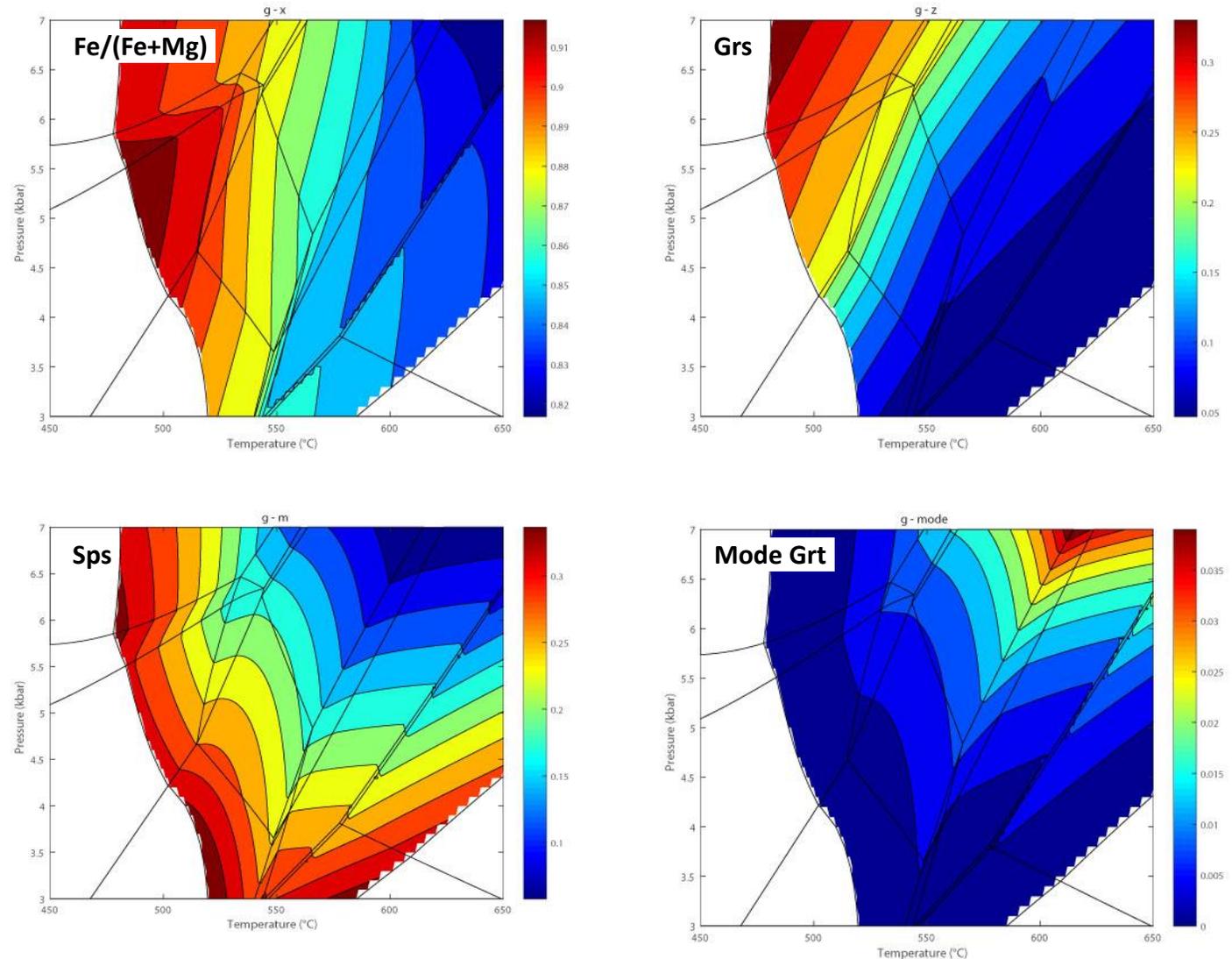
- Template dr-file is provided
- Input data requires some editing
- DRAWPD features:
  - Can define assemblage fields, recommends colouring according to variance
  - Optional: title, numbering of points and curves
  - Does not label axes
- Output as .eps file, editable in a vector graphics program, add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



# Other auxiliary programs

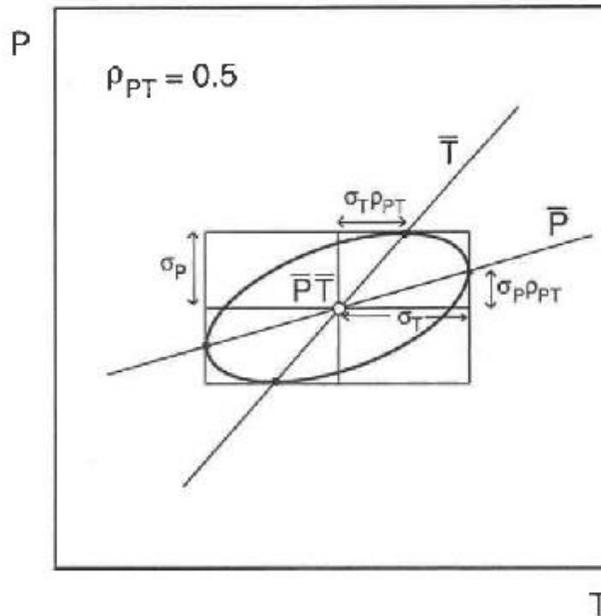
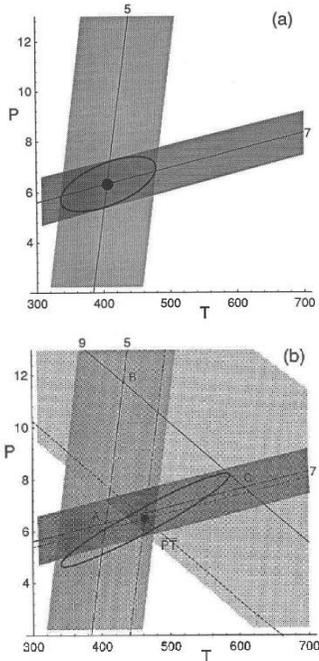
- **AX** – software by Tim Holland
  - Calculates activities for end members from primary analytical data, for use in **average P-T** calculations
  - Uses, or approximates, the then-current solution models
  - With TC v.3.50, users encouraged to use the HPx-eos rather than AX
- **TCInvestigator**
  - 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



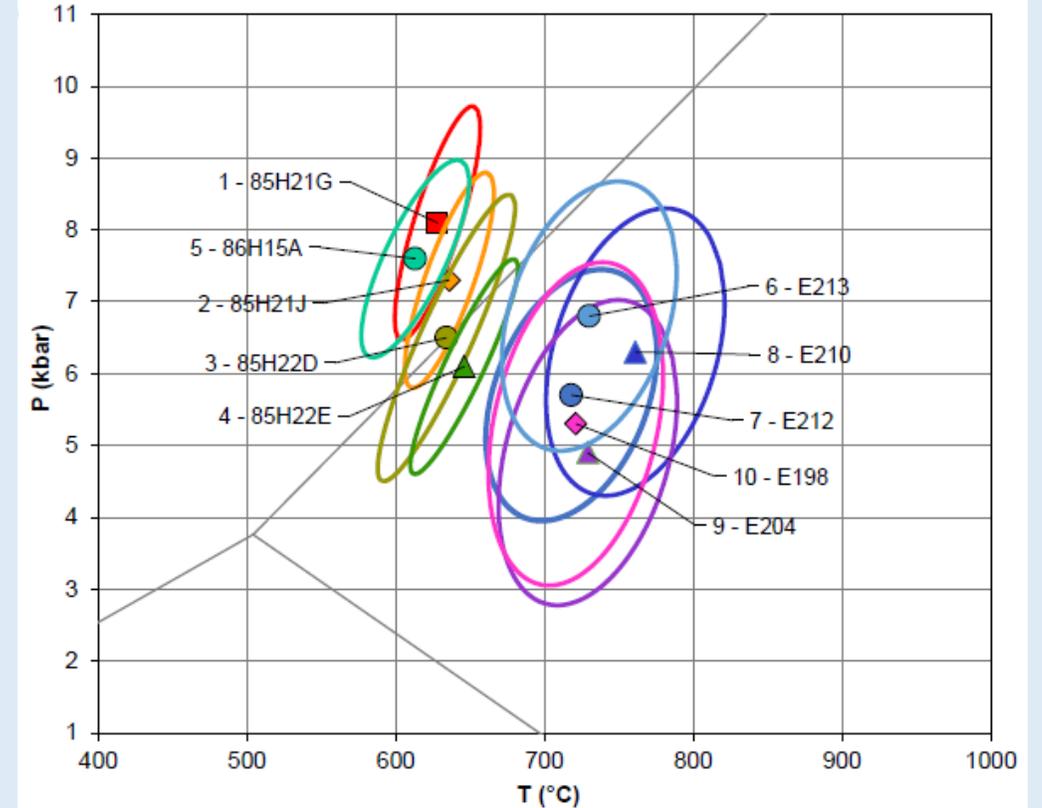
# Mode 2: Thermobarometry – “average $P$ - $T$ ”

- **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  | -0.548 | 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 H2O**

**Independent set of reactions**

1)  $gr + 2ky + q = 3an$

2)  $6mst + 75an = 8py + 25gr + 96ky + 12H_2O$

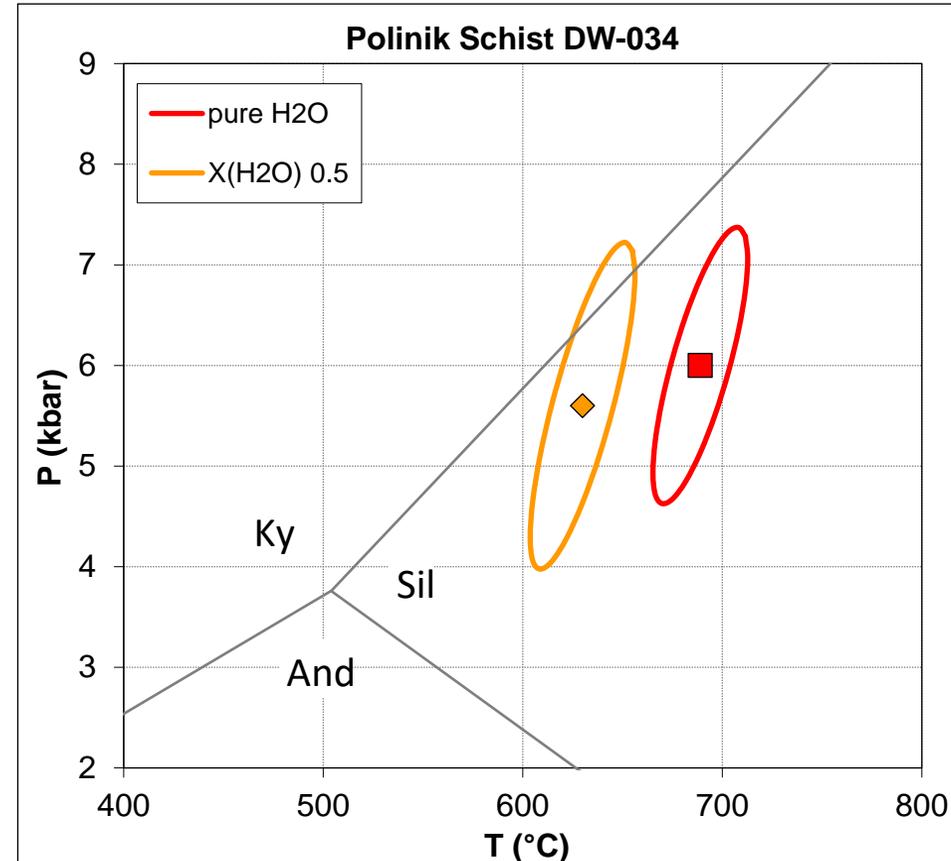
3)  $6fst + 75an = 25gr + 8alm + 96ky + 12H_2O$

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.

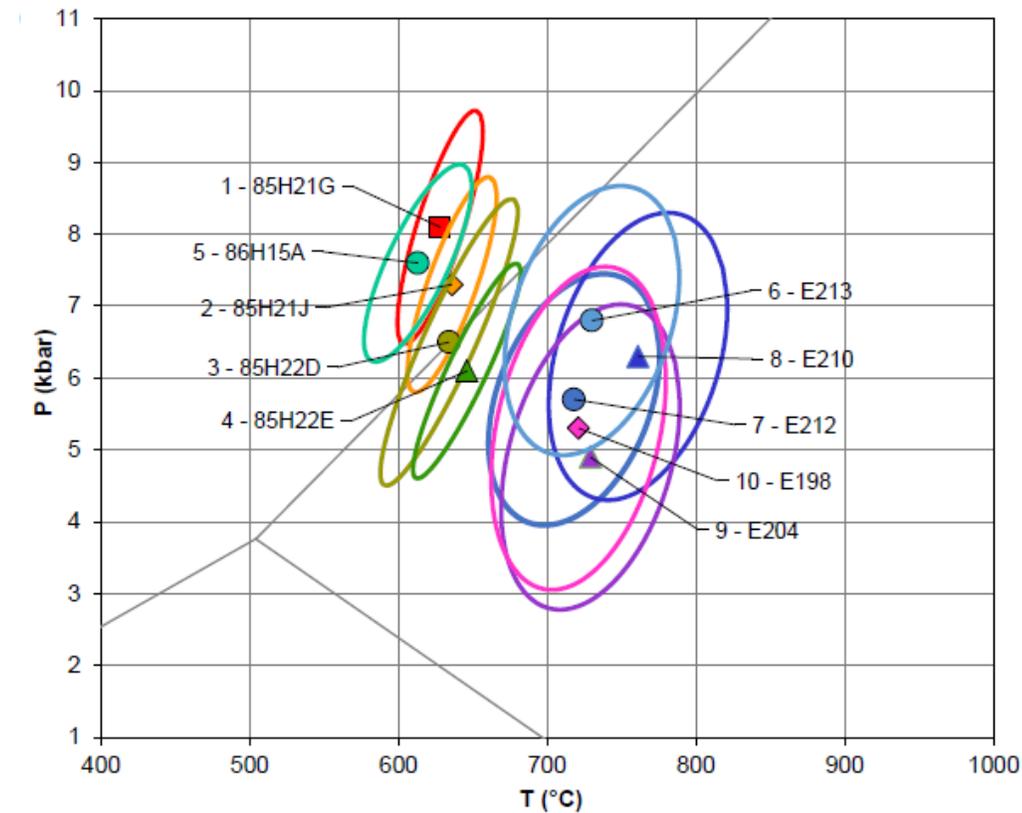
**Consistency with calculated phase diagram is not guaranteed!**

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

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

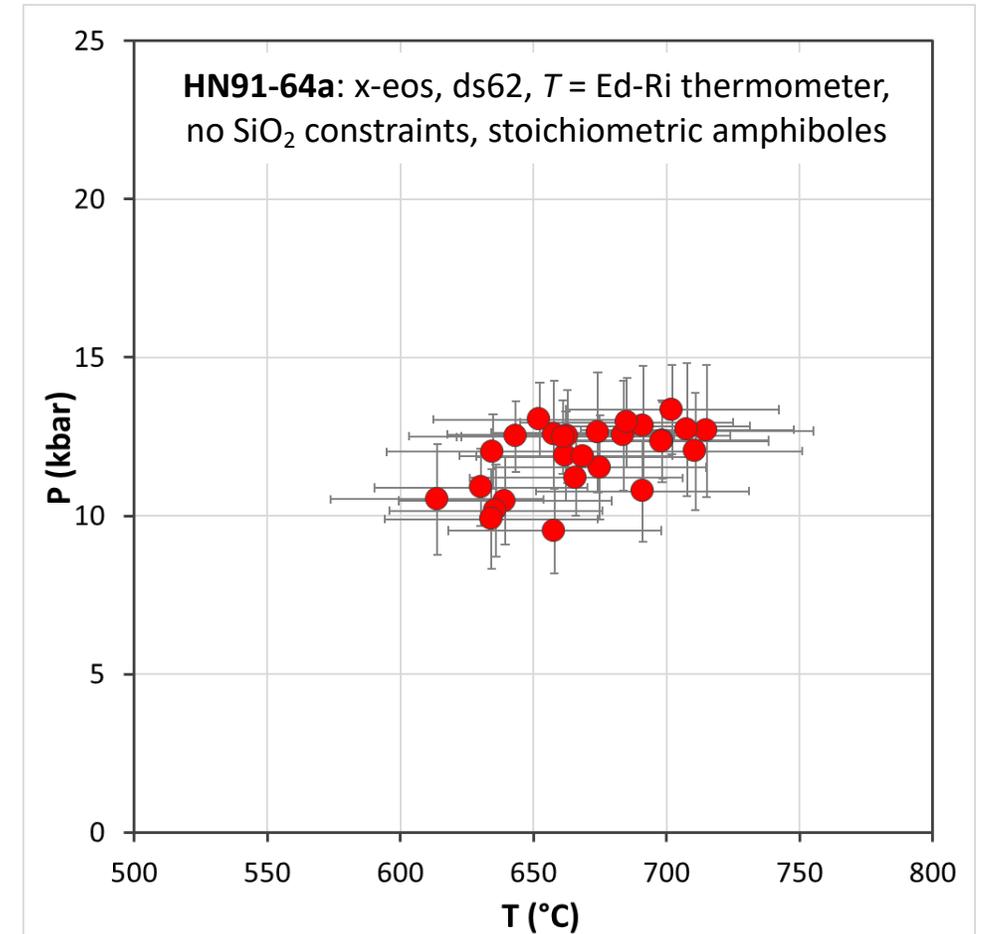
Two groups of samples with different assemblages:

- 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):

- jd + q = abh**
- tsm + 2di + 2q = tr + 2anC
- 7tsm + 2cumm + 14hed + 14q = 7tr + 2grnm + 14anC
- 2prgm + 6abh = tr + tsm + 8jd**
- 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

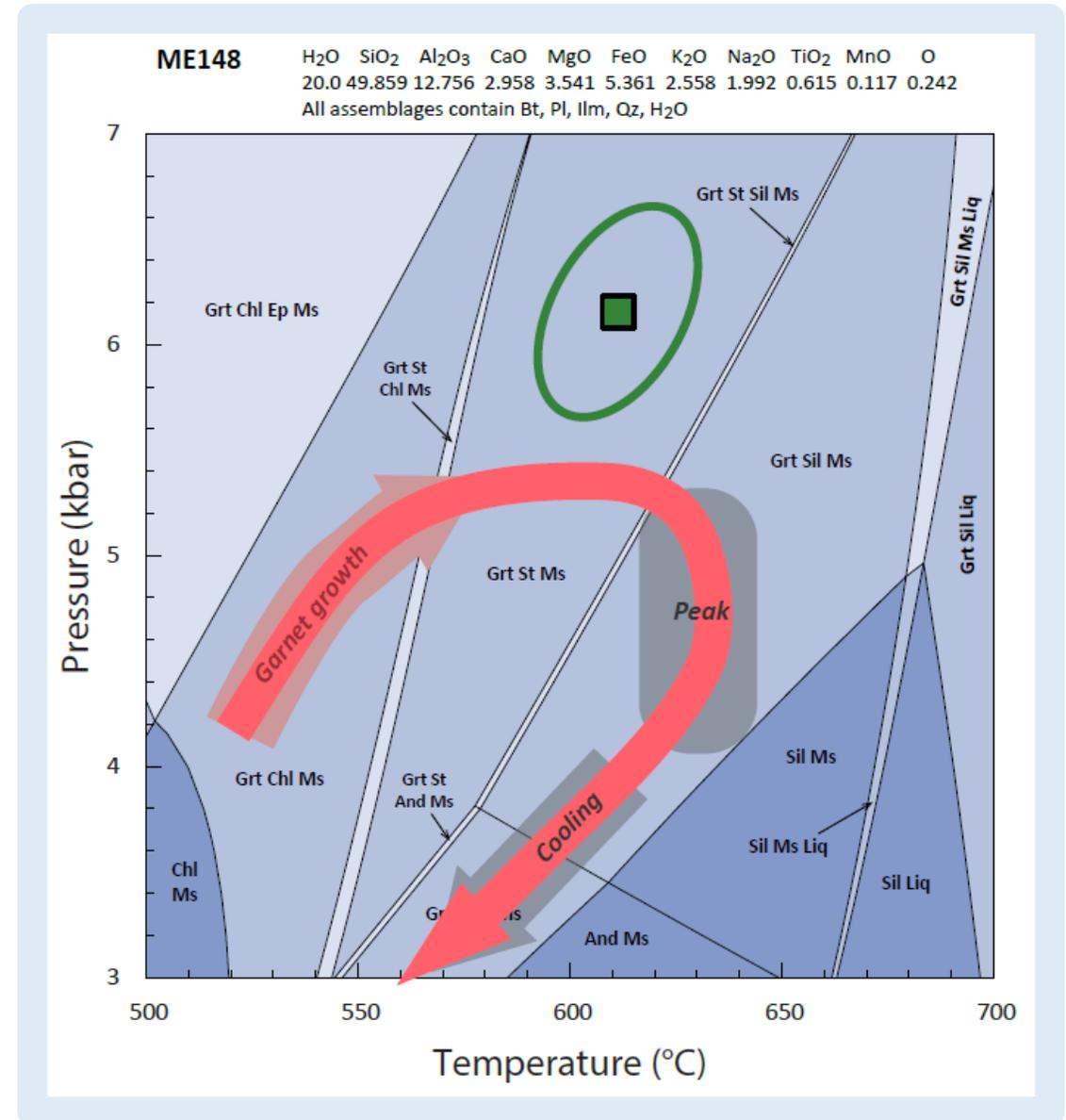
## ▪ Disadvantages:

- 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.