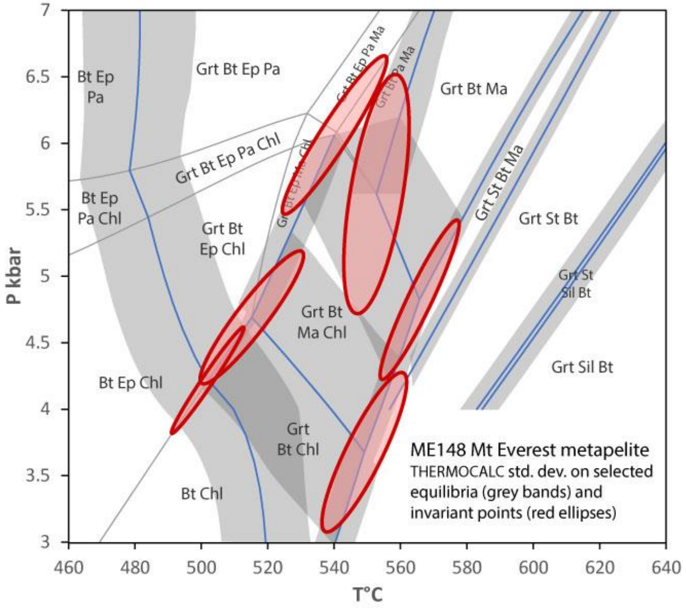
Uncertainties & Best Practices
in
Phase Equilibrium Modelling
and
Thermobarometry



ME148 Mt Everest metapelite

THERMOCALC std. dev. on selected equilibria (grey bands) and invariant points (red ellipses)

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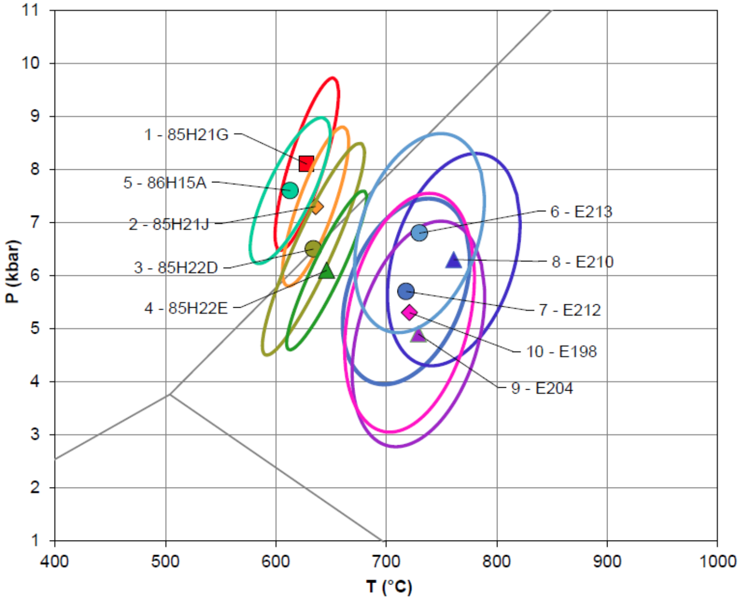


Points to be covered (Wednesday, Thursday)

- Uncertainties: datasets, overall system uncertainties. Random and systematic uncertainty (this session)
- Some thoughts on and examples of best practice in modelling and thermobarometry (this session)
- Bulk compositions (a little here, and detail in Pierre Lanari's talk)
- Departure from equilibrium, kinetics (Pattison/Forshaw)
- Databases & models vs natural record (mostly see Forshaw/Pattison)

This session will, for the most part, assume equilibrium behaviour, and deal with the uncertainty on calculated metamorphic conditions that results from uncertainty or systematic error in datasets and solution models, analytical uncertainty, and sampling bias.

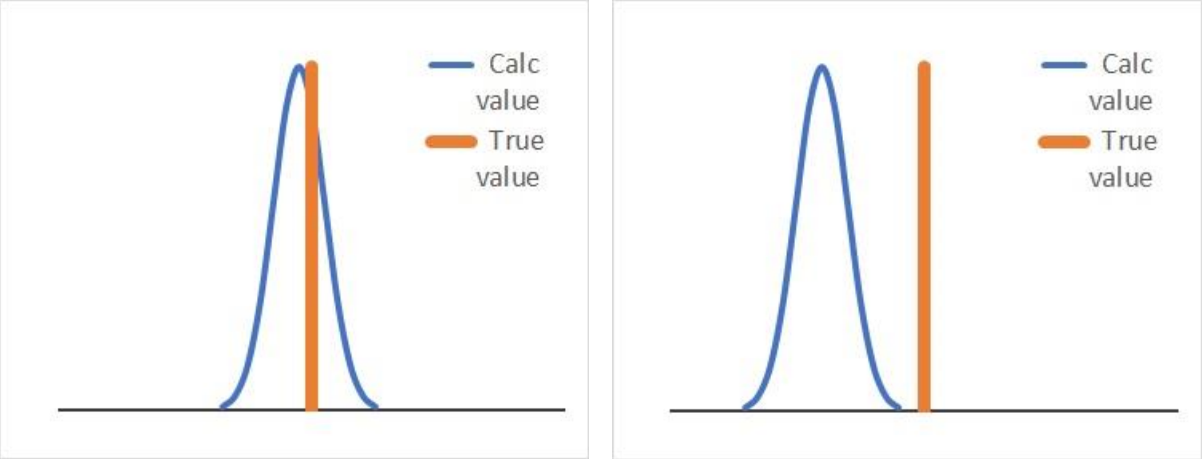
The focus is on the practical application of datasets and calculated phase diagrams in thermobarometry

Examples are all calculated with THERMOCALC, which can provide estimates for some types of uncertainty

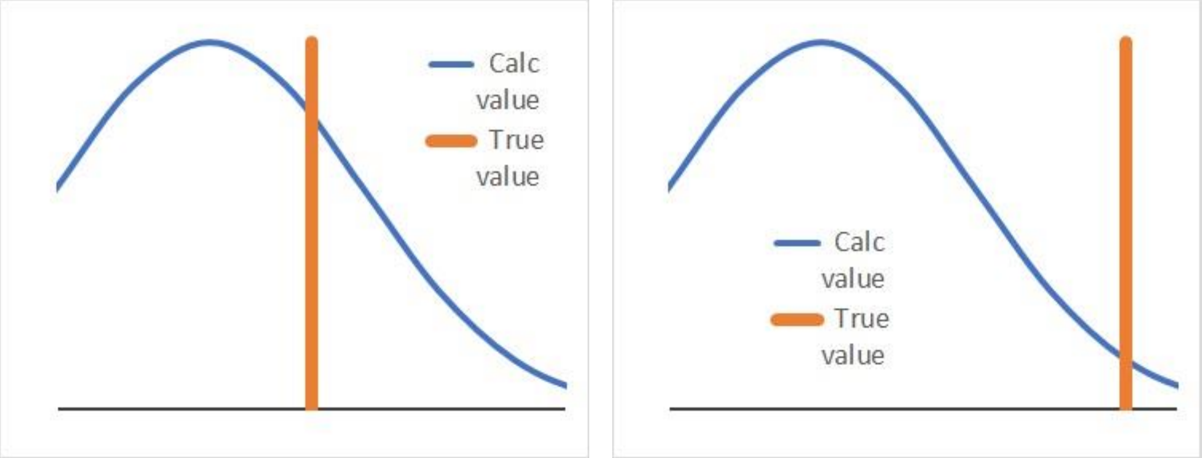
Aspects of uncertainty – random or systematic (bias)

- Random :– treatable as gaussian, there are standard error propagation techniques
- Systematic error :– biased to one side of the 'true' value, for various reasons, e.g., inaccurate experimental value, combining incompatible data, etc.
- Independent or correlated uncertainties? – Dataset enthalpies regressed by least squares (as for HP datasets) are roughly gaussian for an individual value, but highly **correlated** for the dataset as a whole – see discussion in Powell & Holland 1993
- Combining and propagating uncertainties from different sources is not simple
- No statistical formulae today, but instead, concepts, approaches, and implications

Precision and accuracy or random errors:



Precise, and accurate **Precise, but inaccurate**



Imprecise, but accurate **Imprecise, not very accurate**

Thermobarometry: uncertainty in *P-T* calculations

Understanding of the uncertainties on thermobarometry predates modern phase diagram calculation.

This list is adapted from *Practical Aspects of Mineral Thermobarometry* (Waters, 1996, http://www.earth.ox.ac.uk/~davewa/pt/pt05.html)

- **Uncertainty on the thermobarometer calibration**,
  e.g., uncertainty in the position of an end member equilibrium determined by bracketed phase equilibrium experiments. Optimised, internally consistent thermodynamic datasets may be able to estimate this uncertainty.
- **Uncertainty in activity-composition relationships.**
  Depends on an appropriate formulation for the thermodynamic mole fraction, is somewhat less quantifiable. May assume ideal behaviour for a non-ideal phase. Non-ideal models may not extrapolate correctly to the *P, T* or composition range of interest.
- **Analytical uncertainty on the mineral analyses.**
  Derived from counting statistics, standardisation and correction procedures in the electron microprobe. A mixture of treatable random errors and systematic errors.
- **"Geological" error.**
  These are largely systematic errors introduced by us, the petrologists, e.g., in selecting phase compositions which may not be those in chemical equilibrium at the stage of interest in the rock's history.

Overall uncertainty is the sum of all the above errors

Comparison uncertainty concerns our ability to resolve two pressures or temperatures determined using the same calibration of a particular thermobarometer. It depends largely on analytical uncertainty and will be smaller than the overall uncertainty.

The subject is dealt with by Spear (1993), chapter 15, pp. 537-540.

Sources of uncertainty in datasets and models

Fundamental end-member data:

- Experimental data, calorimetry, phase equilibrium studies. Regression and fitting of these for ‘internally consistent’ datasets.
  - Least-squares approach (Holland & Powell datasets, enthalpies only) allows some quantification and error propagation.
    Uncertainties explicit in HP datasets and (optionally) in THERMOCALC output
- Input from natural datasets?

Solution models:

- Are of varied complexity but are inevitably simplifications. What to take into account? Site preferences, ordering, etc.
  - Are they flexible enough, or tolerant enough of natural variation, to handle real analyses?
    Models for complex minerals are ‘works in progress’
- Fitted interaction parameters may have considerable uncertainty, but are interdependent, correlated.

Some uncertainties can be propagated through calculations, and some cannot …

- **Can be propagated** through calculations:
  - Analytical uncertainty, e.g. EPMA counting statistics
  - Regression of thermodynamic properties of end members
  - Fitting of solution model interaction energies
- **Uncertain but not quantifiable**, cannot be propagated:
  - Systematic part of analytical uncertainty e.g. calibration
  - Inappropriate assumptions in recalculation of mineral formulae
  - Inappropriate formulation of activity–composition relationships
  - Incorrect measurement or estimation of end member properties not regressed, e.g. entropies

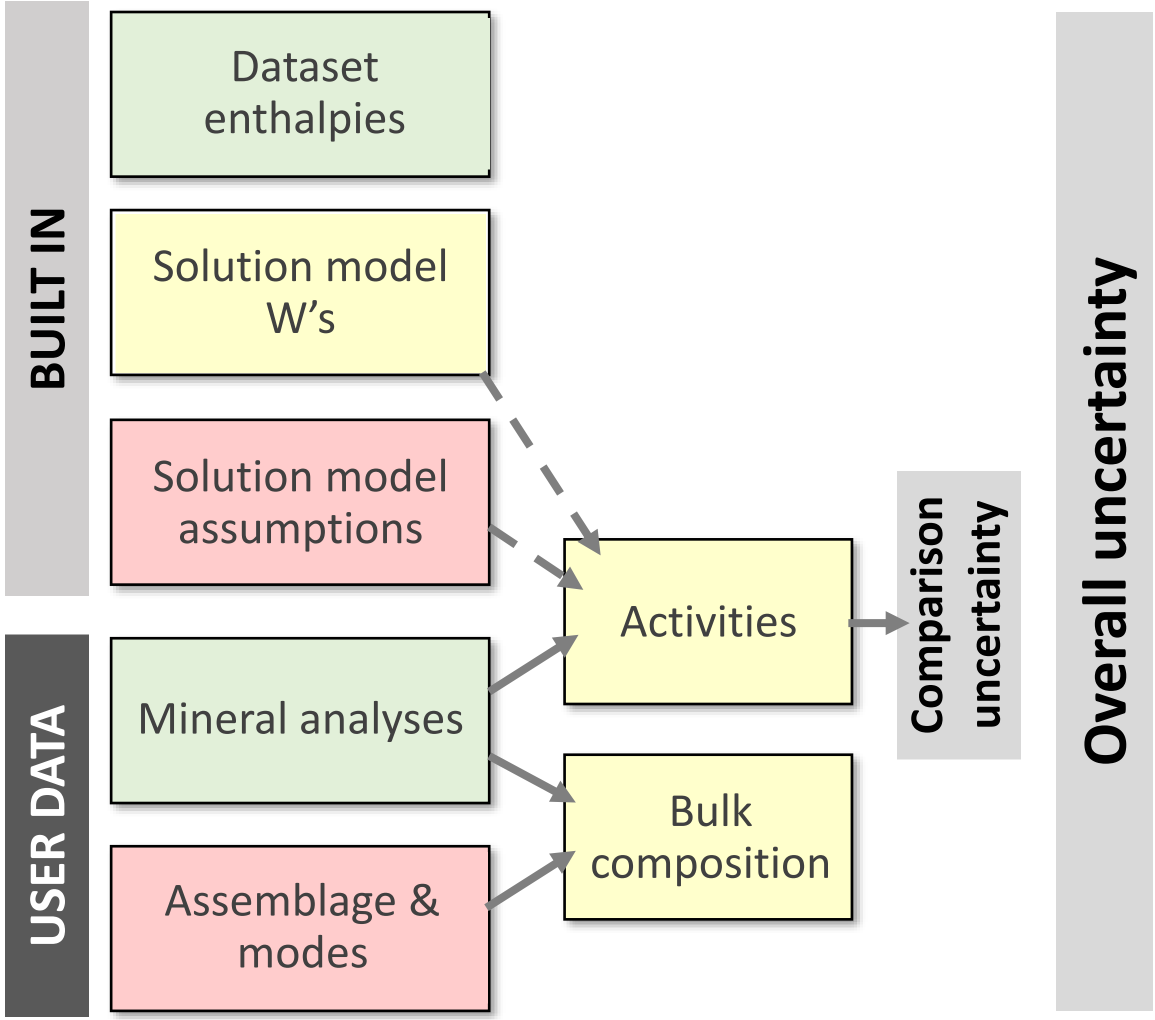
These types broadly correspond to random vs systematic uncertainty. For the second class, Powell prefers to use ‘bias’ rather than ‘uncertainty’.

Sources of uncertainty for thermobarometry

- **Dataset uncertainty** (THERMOCALC)
  - On end member enthalpies, with covariance matrix
    - Quantifiable, propagated
- **Solution model uncertainty** (e.g. HPx-eos)
  - Fitting interaction parameters (W's)
    - Quantifiable, propagated (via activities)
  - Formulation of model (sites, occupancies)
    - Systematic, not quantifiable
    - Affects ability to reproduce natural compositions
- **Analytical uncertainty**
  - From method of mineral analysis, e.g. EPMA
    - Quantifiable, estimated in AX for average *P-T*
- **Sampling (or 'geological') uncertainty**
  - Heterogeneity or bias in assemblage & modes
    - Systematic, not quantifiable
- **Bulk composition uncertainty** (input data)
  - Derives from analytical and sampling uncertainty
    - Maybe semi-quantifiable with Monte Carlo

Class of uncertainty:

green = quantifiable; yellow = partly quantifiable; red = mostly systematic



“On Thermobarometry”

Much of what we do is directed at thermobarometry: equilibrated conditions, or a record of changing conditions

Currently, two approaches:

1. **Inverse modelling** – “conventional thermobarometry”
   - Use compositional data from equilibrated minerals
   - Determine *lnK* for calibrated/calculated equilibria
   - Find best-fit of equilibria in *P* and *T*
2. **Forward modelling** – calculated phase diagrams
   - Define chemical system to use
   - Provide a bulk composition for rock sample of interest
   - Calculate mineral assemblage fields
   - Calculate mineral composition isopleths
   - Calculate mineral proportions
   - Use any/all of these to locate the natural rock in *P-T(-X)* space

- **Powell R & Holland TJB (2008). On thermobarometry.** *J Metamorphic Geology*., 26, 155-179.
  Some key statements in advocating phase diagram thermobarometry …
  - The rock’s bulk composition provides additional information on P-T conditions, by constraining the extent of mineral and assemblage stability
  - Assemblage fields can be contoured for mineral compositions, and mineral proportions (modes)
  - To be compatible, conventional thermobarometry (inverse modelling) should use the same dataset and solution models as for phase diagram calculation (e.g., as in avPT)
  - This will require recalculation of mineral analyses for compatibility with solution models: the ‘**ideal analysis**’ concept involves finding an analysis that has exact stoichiometry (according to the model) and (if required) an appropriate estimate of Fe^{3+}, and is as close as possible to the natural mineral analysis.

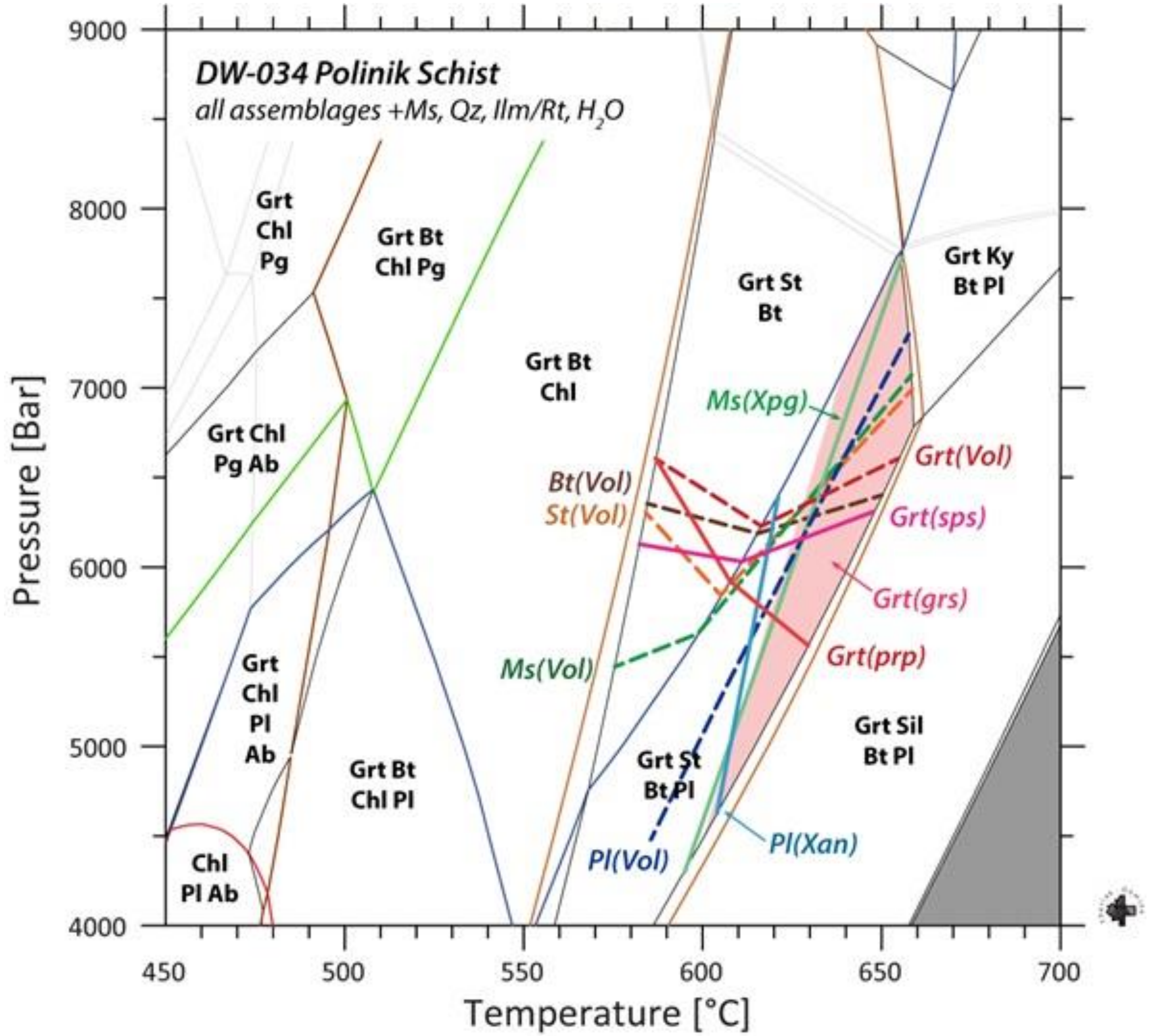
Using phase diagrams for thermobarometry

- Match assemblage field
- Use mineral composition isopleth intersections
- Match modal proportions

These are interrelated by *P-T-X-M* (cf. Spear 1993)
But note this hierarchy of dependencies: -

1. Mineral composition isopleths (depend on fundamental end-member equilibria in the relevant assemblage)
2. Mineral mode contours (equilibria plus bulk composition constraint, with its own uncertainties)
3. Assemblage field boundaries (equilibria plus bulk comp, plus a dependence on free energy difference between adjacent assemblages near their boundary)

Intersection of composition and mode isopleths



Dataset uncertainties in THERMOCALC

THERMOCALC allows the standard deviation on curves and points to be calculated from the dataset covariance matrix of best-fit end member enthalpies.

These are **dataset uncertainties** (with a contribution from solution models)

Enabled by setting script “calcsdnle yes”

Examples of dataset uncertainties (**one** std dev), at/above garnet isograd with Bt, Chl, Pl Ms Qz:

1. Composition isopleths:

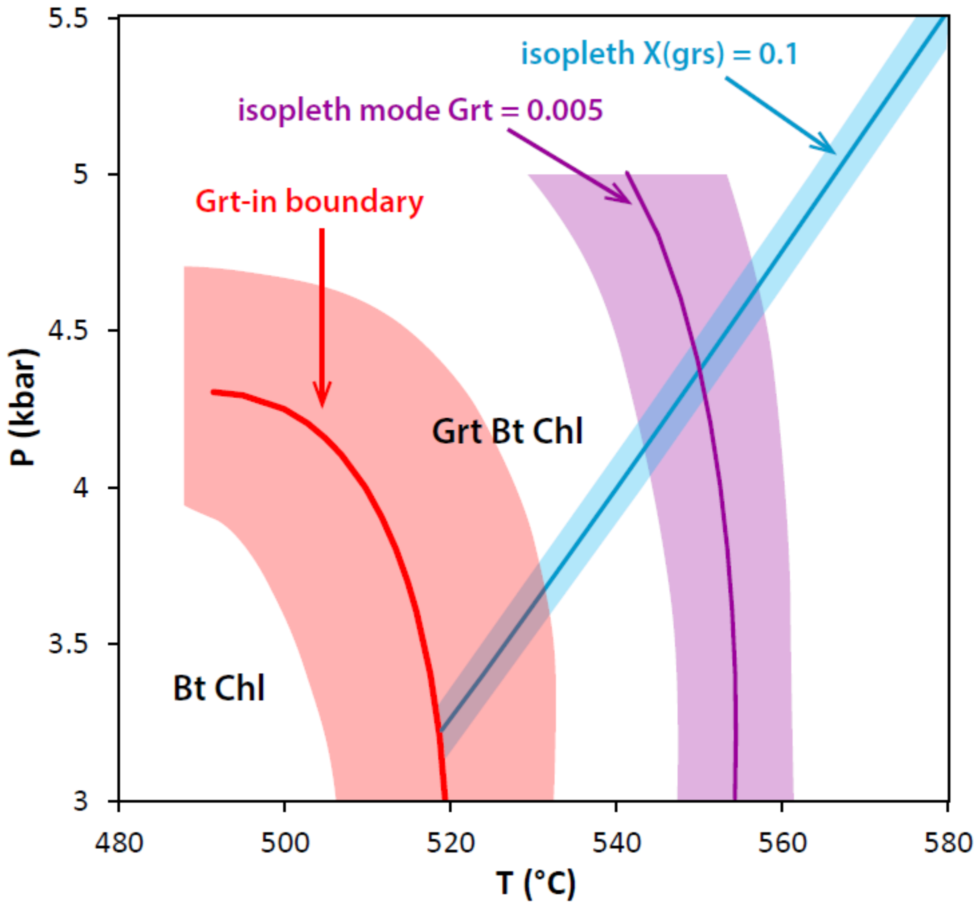
Isopleth X(grs)	± 3 °C

2. Mineral mode contours:

Mode garnet	± 7 – 10 °C

3. Assemblage field boundaries

Garnet isograd	± 12 – 20 °C



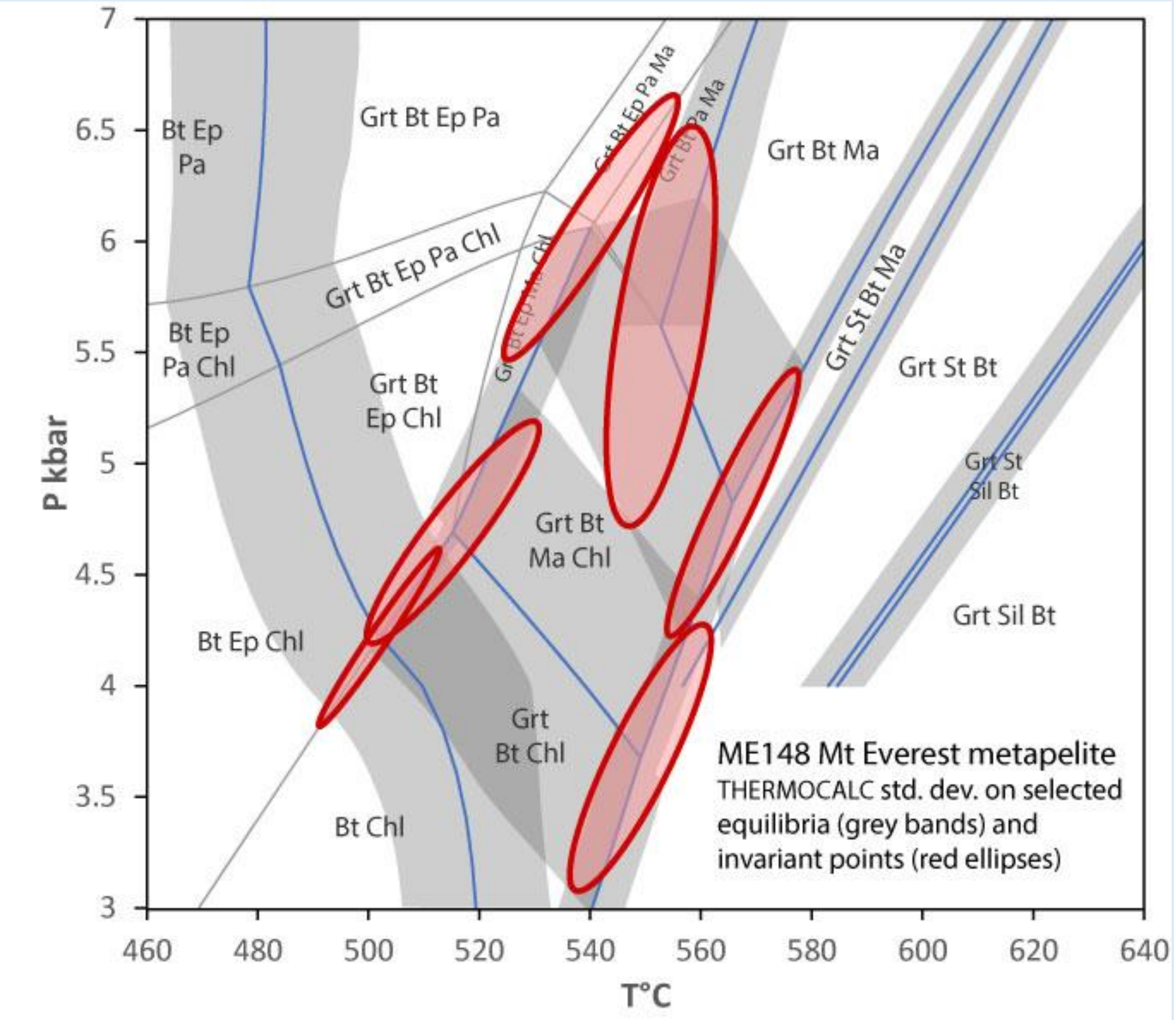
Dataset uncertainties on assemblage field boundaries

ME148 Mt Everest metapelitic schist phase diagram (calculated with tc3.50, DS6.2, system MnNCKFMASHTO)

Note the large uncertainty on the garnet-in equilibria, and even wider bands on some margarite-bearing fields.

Curves relating to isograd reactions for epidote-out, staurolite-in and sillimanite-in have significantly smaller uncertainty.

The uncertainties are not independent. Where bands or ellipses overlap, it does not imply that the topology of the diagram may change, within error, because of the strong correlations in the dataset.

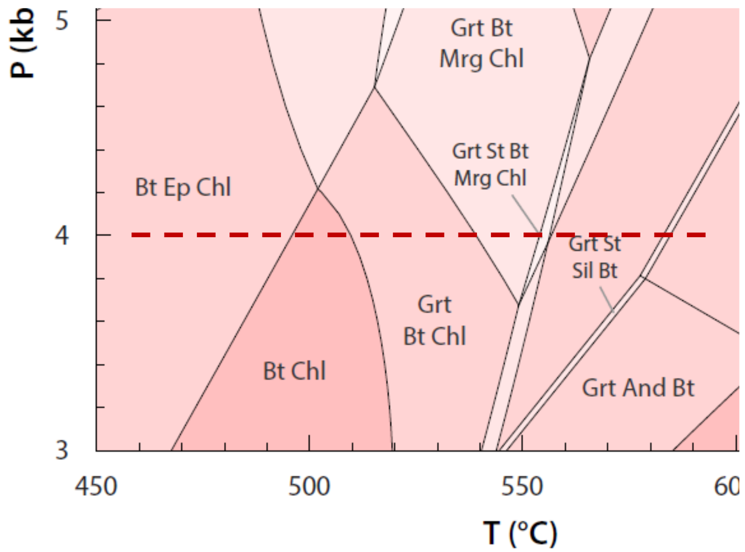


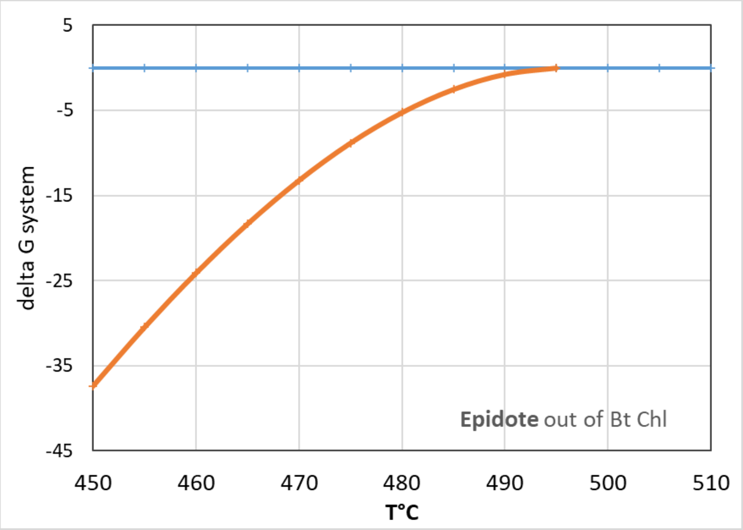
Sensitivity of assemblage field boundaries

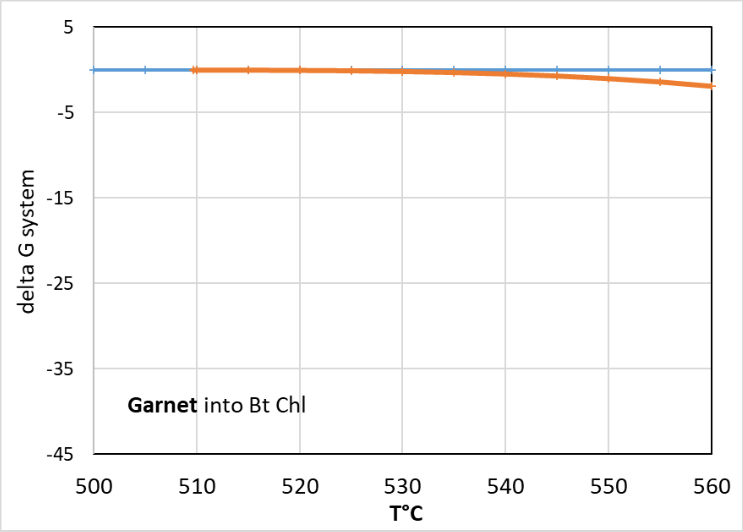
Sensitivity of boundaries should be related to bulk free energy differences between adjacent assemblages.

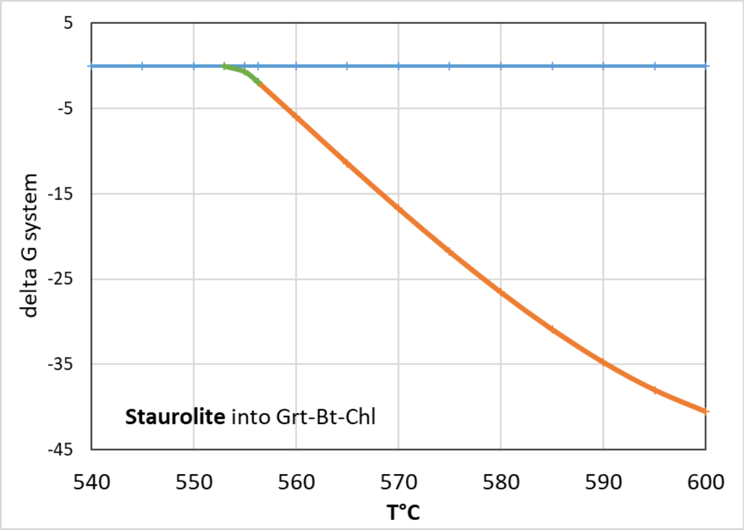
Calculating metastable states is easy in THERMOCALC. System free energy relative to the higher-variance assemblage is shown here, at 4 kbar, for three isograd reactions, plotted at the same scale (other phases, Mrg, Sil, ignored)

Garnet-in reaction, a continuous reaction, small amount of product, is an order of magnitude more sensitive in energy terms









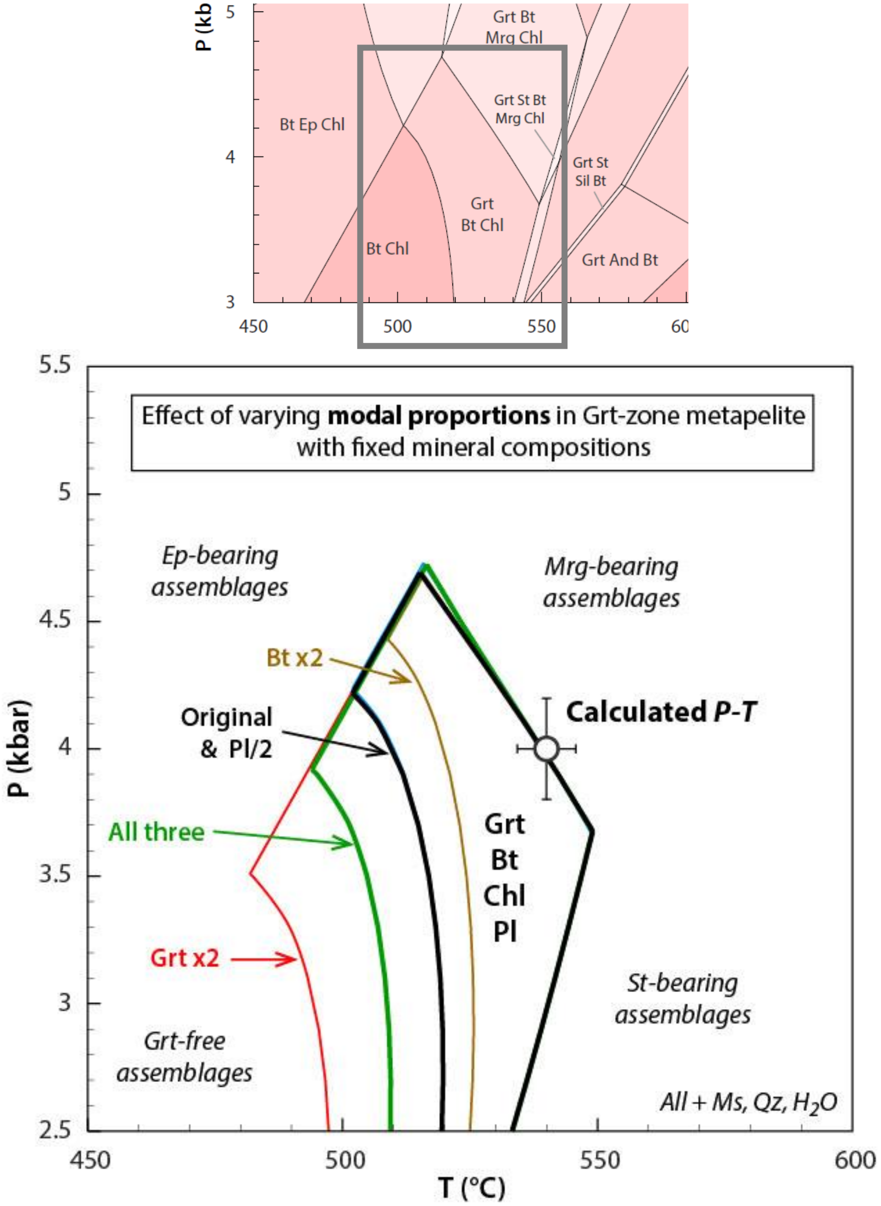
Variation of modal proportions

A ‘controlled experiment’: a garnet-zone rock with known mineral compositions but uncertainty over modal proportions of key phases garnet, biotite, plagioclase.

Assemblage in MnNCKFMASHTO has variance 5

- Calculated *P-T* with initial bulk composition is 4 kbar, 540°C
- Doubling amount of garnet enlarges assemblage stability field, T of garnet ‘isograd’ lowered by ~25°C
- Doubling amount of biotite reduces stability field by 5–10°C
- Halving of amount of plagioclase (~25% to ~13%) has no effect on garnet stability, minor effect on margarite-in curve
- Net effect of all 3 simultaneous changes is also shown

Calculated *P-T* lies on or just over the margarite-in boundary – but recall that this boundary has large dataset uncertainty.



How should phase diagrams be used for thermobarometry?

What to match? Assemblage field; mineral composition isopleth intersections; modal proportions?

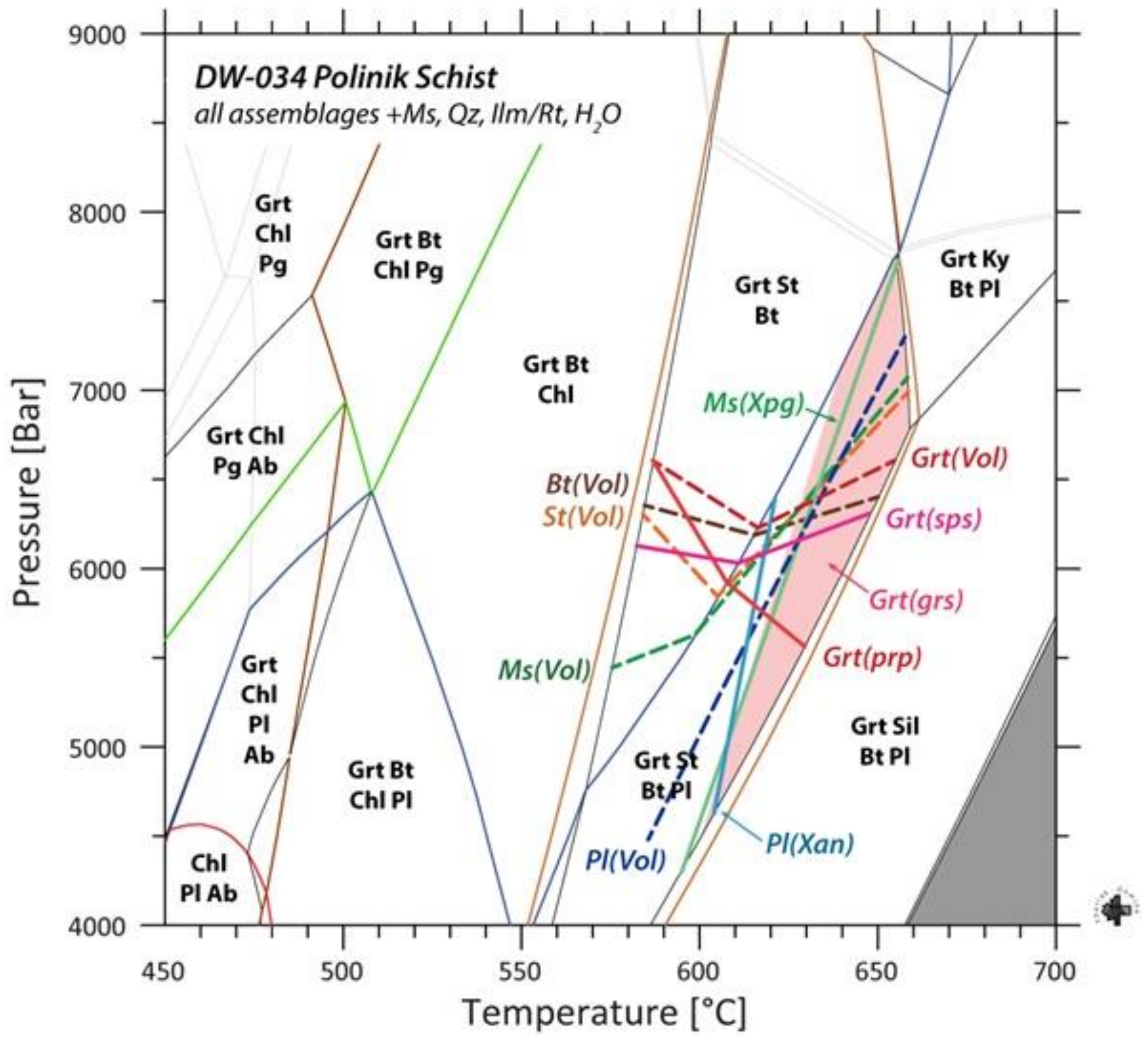
- **Thermobarometry viewpoint**
  – mineral composition isopleths best, if falling in field of observed assemblage

  Note that Eleanor Green & Roger Powell are now looking at a method for optimising ***all*** isopleth intersections, i.e. adding a role for bulk composition control and mode isopleths

- **Refining dataset and models**, (i.e. how accurate is the diagram you're using, can it be improved?)
  – getting the phase boundaries right is 'best', provided fundamental data are already optimised to give phase compositions within valid uncertainty limits.

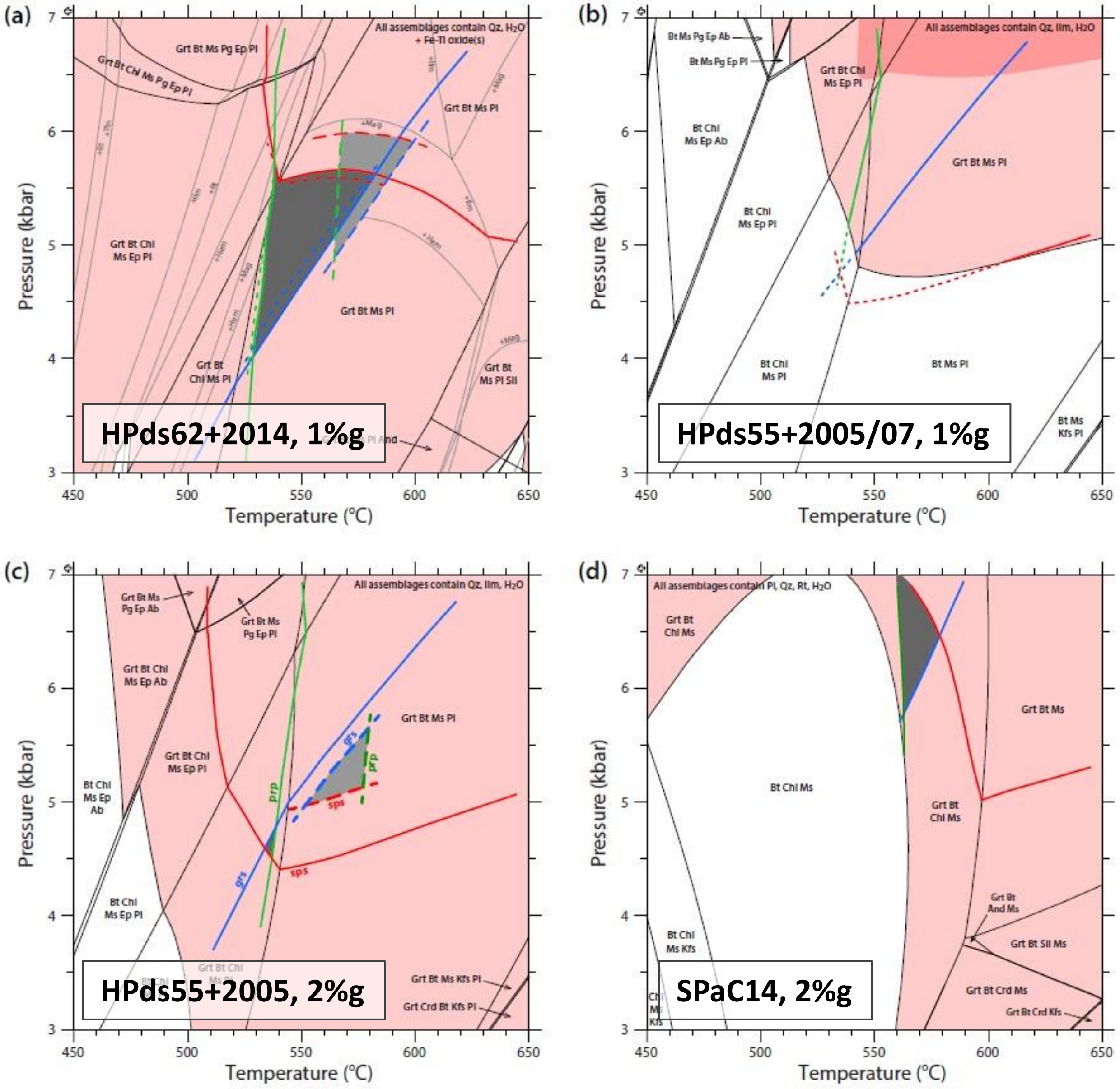
  However,
  if underlying dataset and solution models contain errors, fitting phase boundaries will introduce *compensating* errors, affecting *both* phase compositions *and* modal proportions

Intersection of composition and mode isopleths

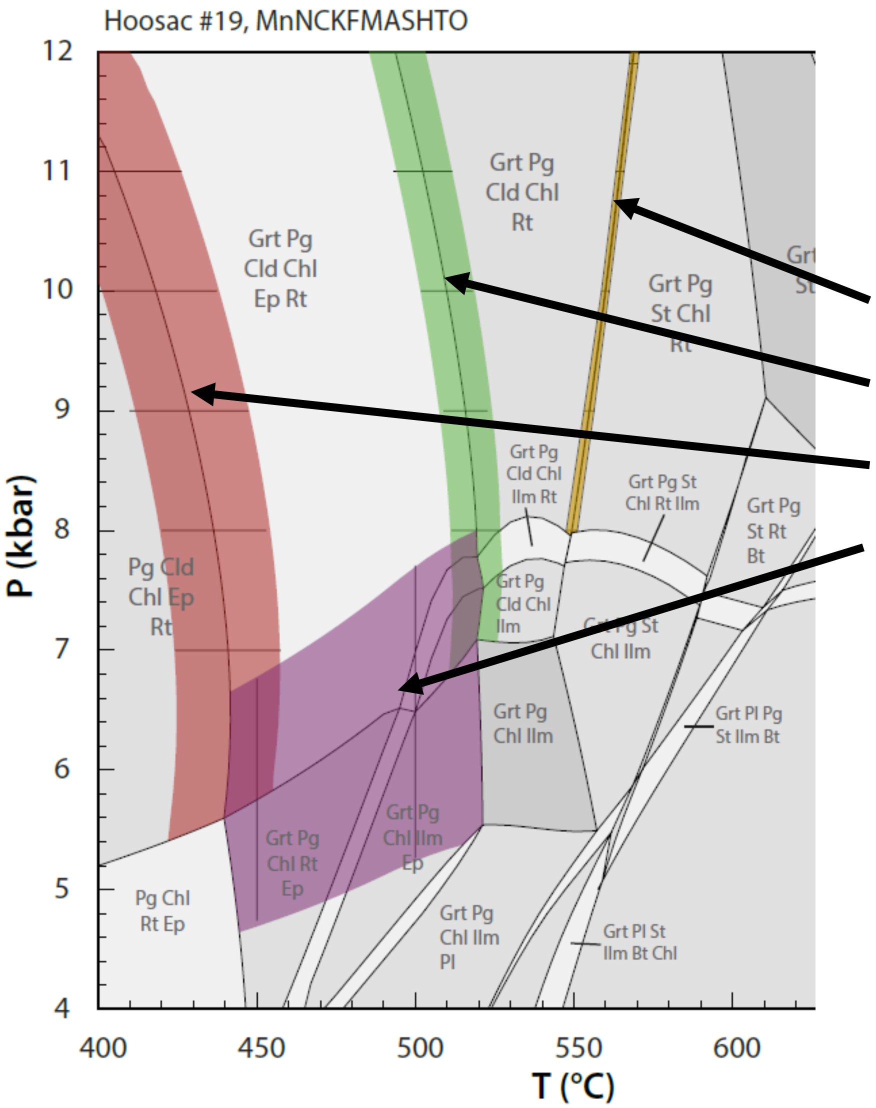


Using different datasets and models – garnet stability

- Garnet stability as a function of dataset and bulk composition (Fig.3 from Waters, 2019)
  One rock, two bulk compositions differing only in amount of garnet (1 vol% or 2 vol%), three datasets.
  - (a) HP ds62, 2014 models, 1% garnet
  - (b) HP ds55, 2005 & 2007 (darker), 1% garnet
  - (c) HP ds55, 2005 models, 2% garnet
  - (d) SPaC14, simple models, 2% garnet
- Note that garnet composition isopleths for pyrope and grossular are not significantly displaced
- However, the isopleth for *spessartine* in garnet varies in position, as it is sensitive to the amount of garnet relative to other Mn reservoirs
- In e.g. (a), a wide zone of Grt at low T can contain a very small amount of Mn and/or Ca-rich garnet, not always seen in practice



Dataset uncertainty vs sampling uncertainty



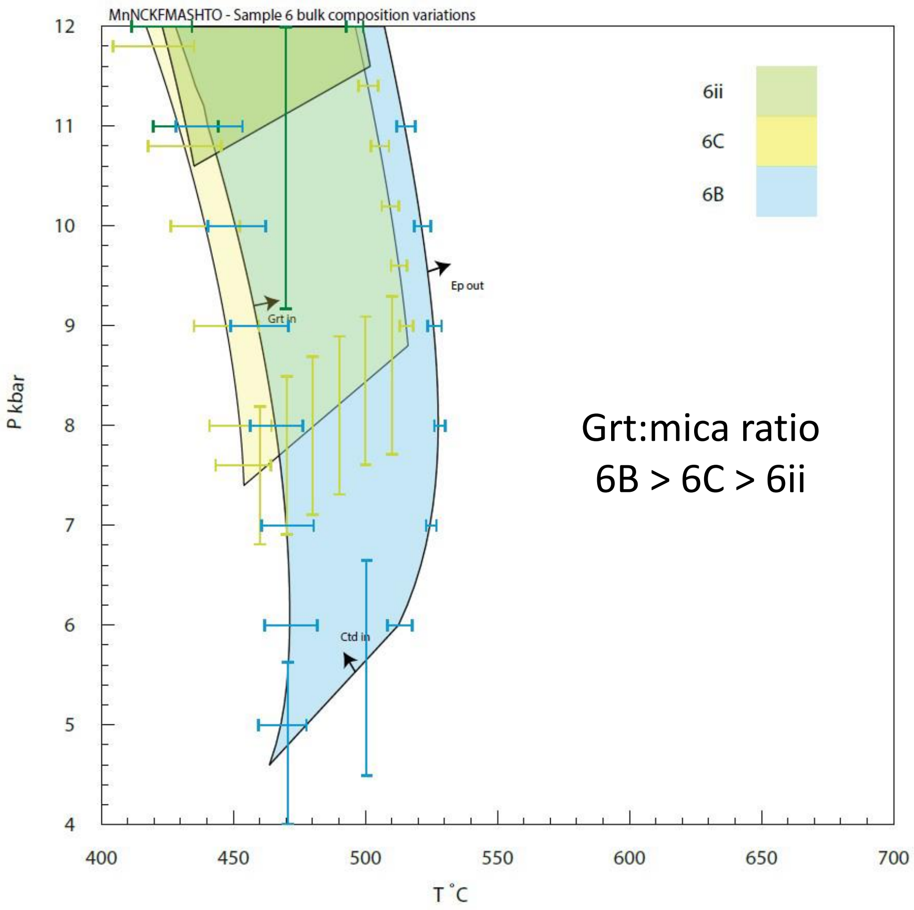
Hoosac schist example

Coloured bands show dataset uncertainty (enthalpies) on assemblage field boundaries:

- St-in (orange)
- Ep-out (green)
- Grt-in (red)
- Cld-in (purple)

Note the variation.

(From Anna Bidgood MS thesis)



Grt:mica ratio
6B > 6C > 6ii

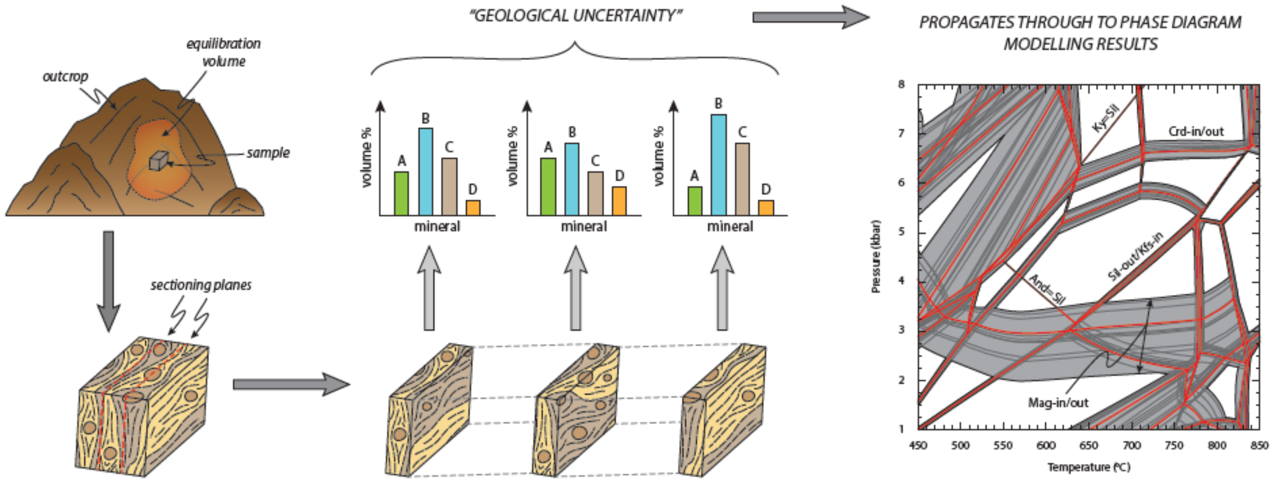
Extent of the Grt-Cld-Chl-Ep field, in 3 modelled thin sections of the same sample (Hoosac #6), illustrating probable random error associated with inhomogeneity at the sampling scale

“Geological uncertainty” (Palin et al. 2016)

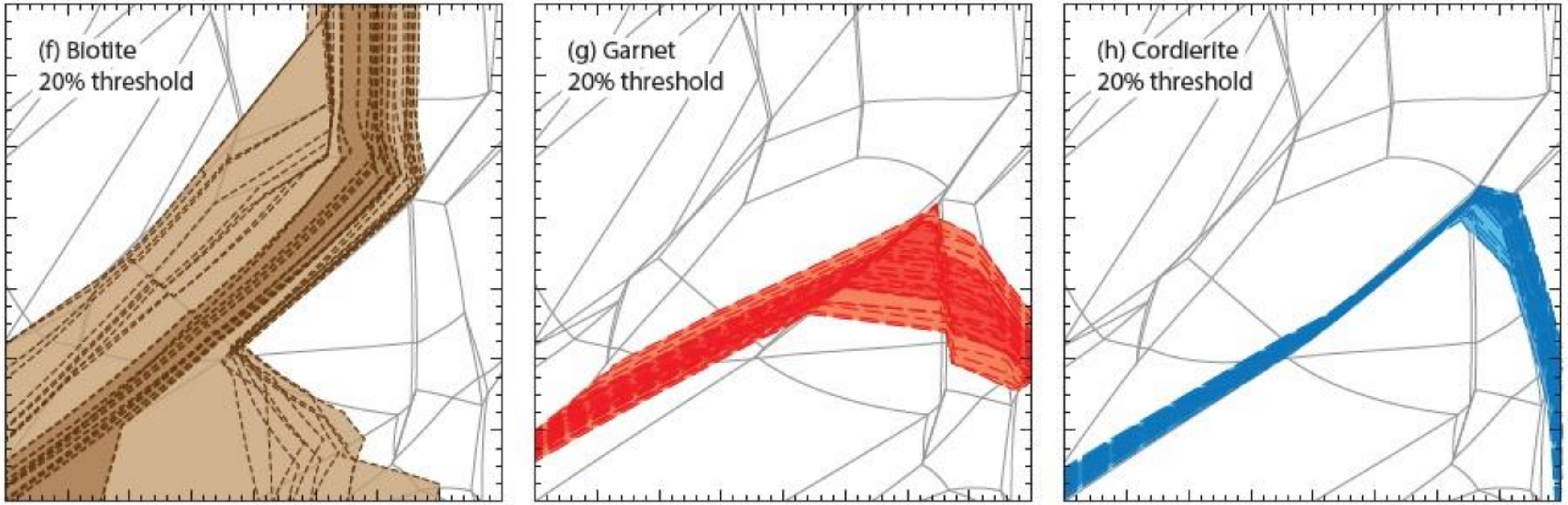
The Danba metapelite example – heterogeneity (this is not about ‘scale of equilibrium’, just sampling bias)

Top right diagram shows effect on principal assemblage boundaries in the phase diagram

Below are the effects on mode isopleths of biotite, garnet and cordierite resulting from Monte Carlo perturbation of the original modal proportions of minerals.



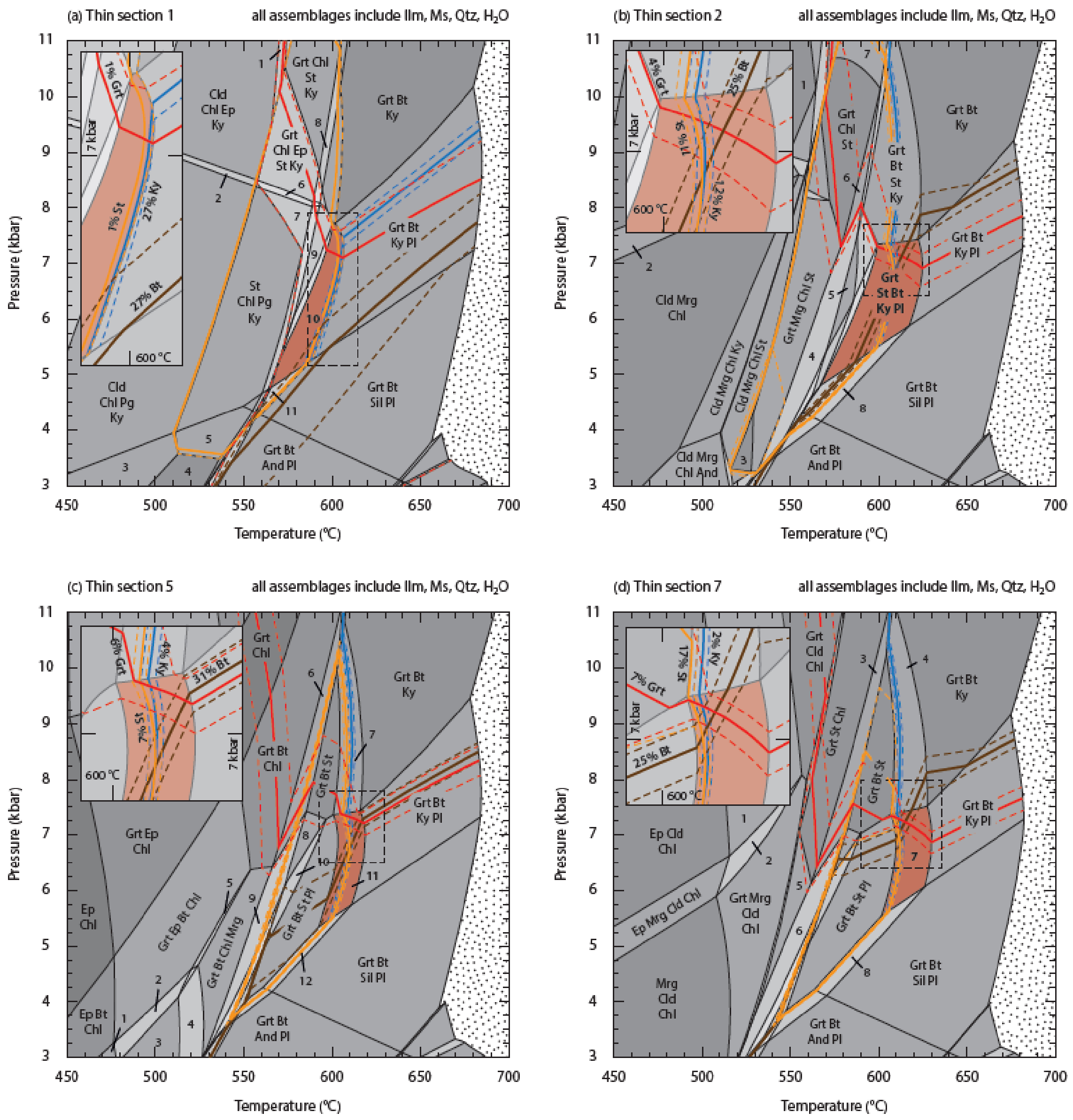
Random perturbations of modes do not produce a Gaussian distribution of displaced curves.

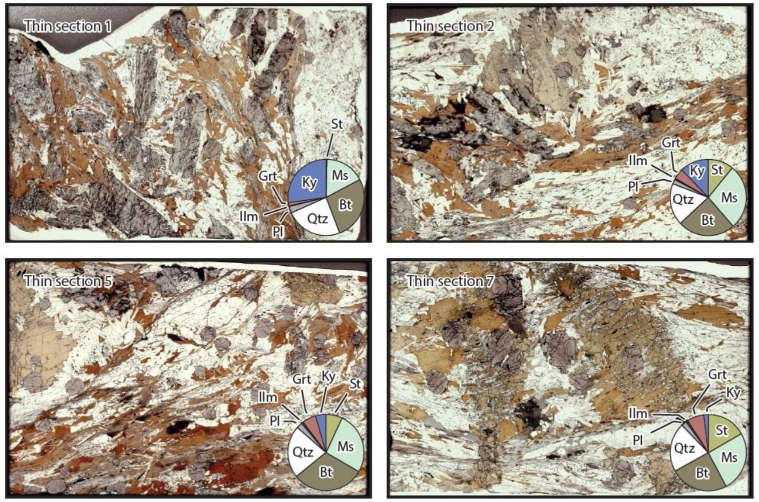


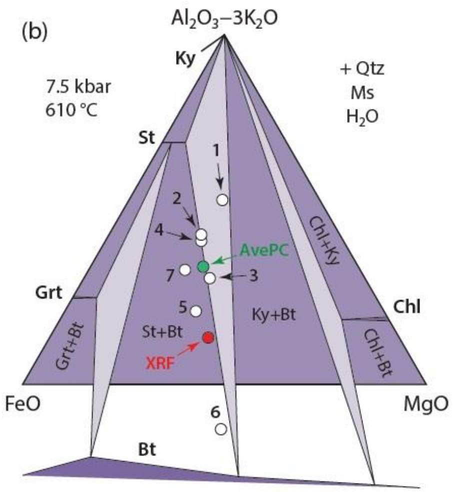
“Geological uncertainty” (Palin et al. 2016, JMG)

The Danba example – heterogeneity in a porphyroblastic rock
Results from different thin sections of the same sample, with dramatically different modal proportions, bulk compositions, and some different assemblages.

Diagrams differ significantly, but all samples have isopleth intersections that give essentially the same *P-T* result at ~7 kbar, 600–630°C







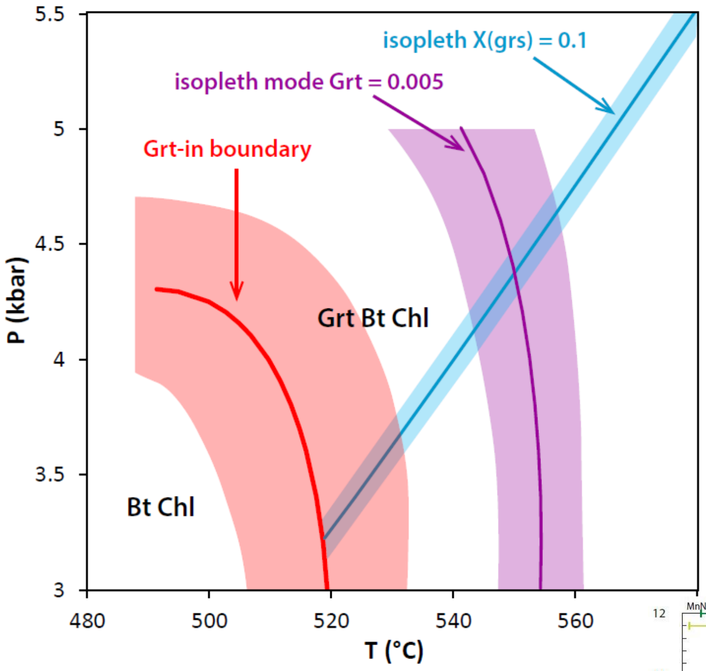
Summary of uncertainty in forward modelling

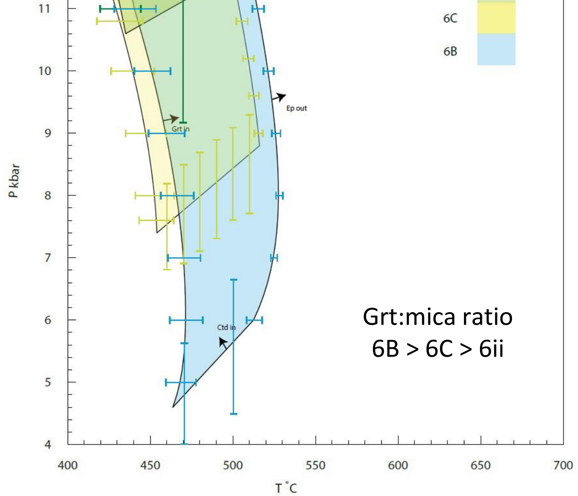
Contributions to overall uncertainty

- Dataset (+ solution model) uncertainty
  Use THERMOCALC to estimate
- Sampling uncertainty
  Under user control/lack of control, can be large
- Analytical uncertainty
  User control, mix of random & systematic
- Sampling + Analytical = Bulk composition uncertainty

Note hierarchy of uncertainties affecting P-T location

1. Composition isopleths
   relatively robust
2. Modes
   have additional dependence on bulk composition
3. Field boundaries
   additionally sensitive to free energy difference (change with *P*,*T*) between the two adjacent assemblages





Grt:mica ratio
6B > 6C > 6ii

Thermobarometry by inverse modelling (avPT)

Uncertainty on average P-T calculations

Dataset uncertainty

Is treated as before, from correlated enthalpies

Analytical uncertainty

Natural mineral formula recast into end members

Activities calculated from mixing-on-sites and interaction parameters (at initial PT guess)

Treated by considering uncertainty on activities of end members

Uncertainty on activities: model in Powell & Holland (1988):

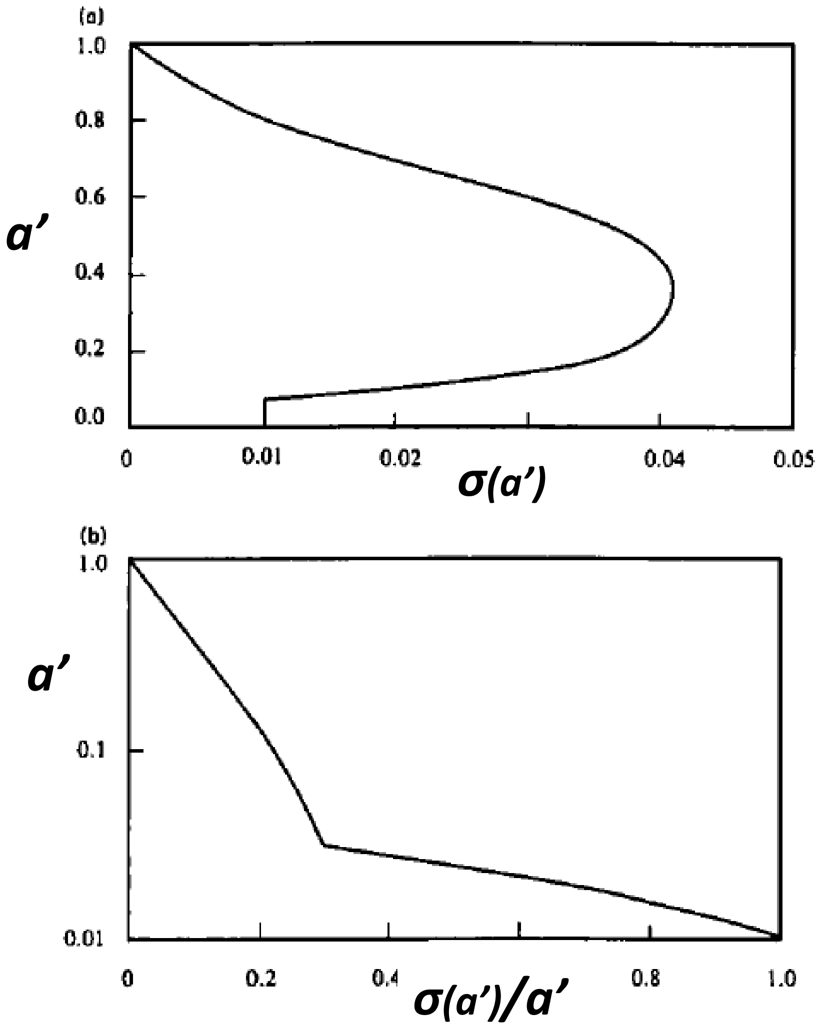
General scheme reflects the multiplicity of the site dominantly responsible for the activity, and factors in the value and uncertainty of the relevant solution model interaction energy, giving a value for the standard deviation on activity – functions graphed opposite.

Small mole fractions are treated differently, to prevent σ→ 0.

Different scaling factors for are used for overall and comparison uncertainty

Powell & Holland 1988 Fig. D1

a’ is a one-site-normalised activity



Uncertainty in average *P-T* calculations (inverse modelling)

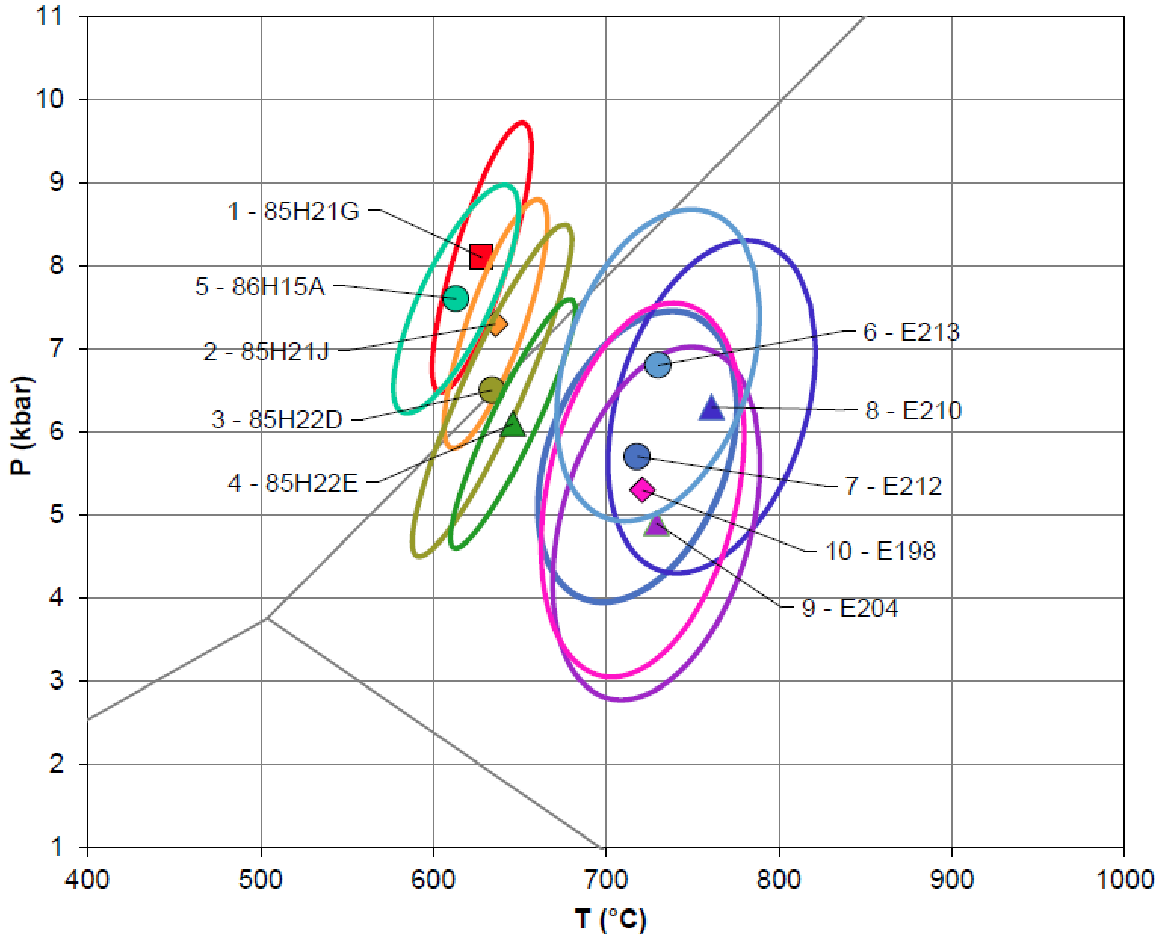
Dependence of *P-T* precision and correlation on mineral assemblage and other factors

Two groups of samples from across the MCT zone and Greater Himalayan Sequence south of Mt Everest (data from Simpson 2002 thesis, Searle et al. 2003).

Narrow ellipses in lower-*T* group are muscovite-bearing, shape and position controlled by devolatilization equilibria

Larger, broader ellipses are Sil-Kfs zone migmatitic rocks, lacking muscovite, fewer precise equilibria.

- A water activity (0.4) had to be assigned in these suprasolidus rocks.
- Assuming H_2O activity = 1 generates unreasonable *T* of around 850°C. There are several examples in the older literature



Overall vs relative uncertainty

For a set of samples with the same mineral assemblage (or sub-assemblage):

a) Dataset uncertainty and solution model uncertainty are the same for all

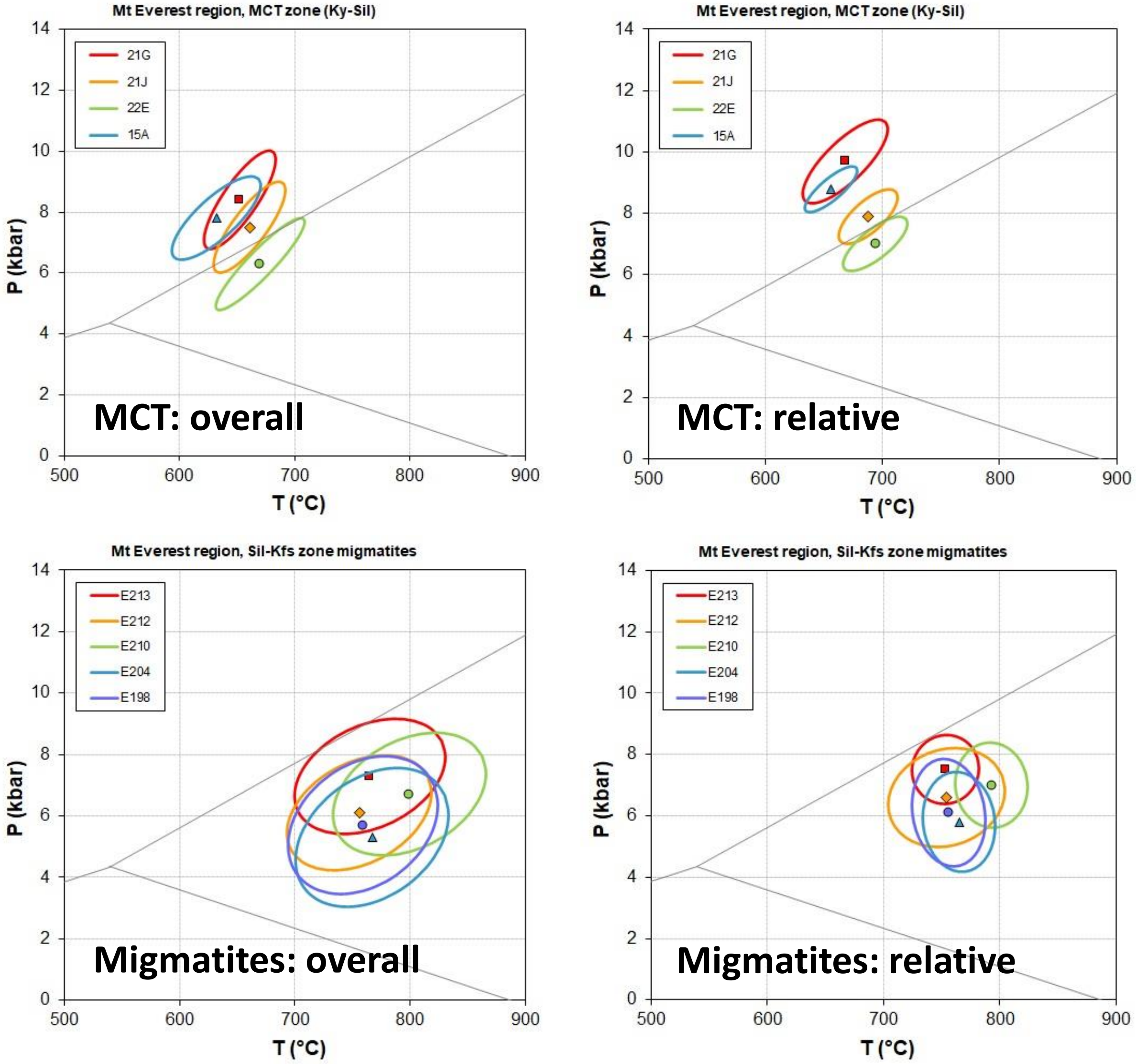
b) Analytical uncertainty can be estimated and propagated

c) Sampling/geological uncertainty remains unquantifiable

So, we can calculate average *P-T* (or average *P*) using just the propagated uncertainty on activities of end members

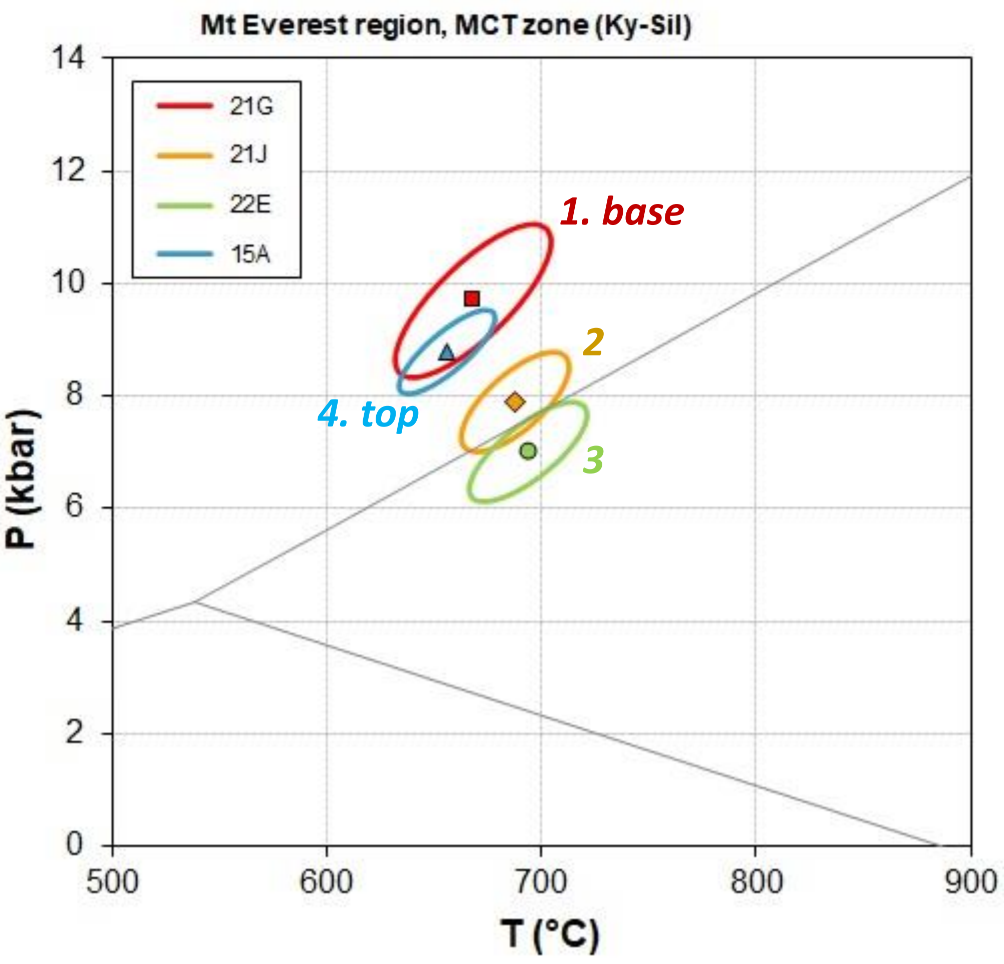
= Relative thermobarometry

Overall vs relative PT ellipses for Himalayan metapelites & migmatites

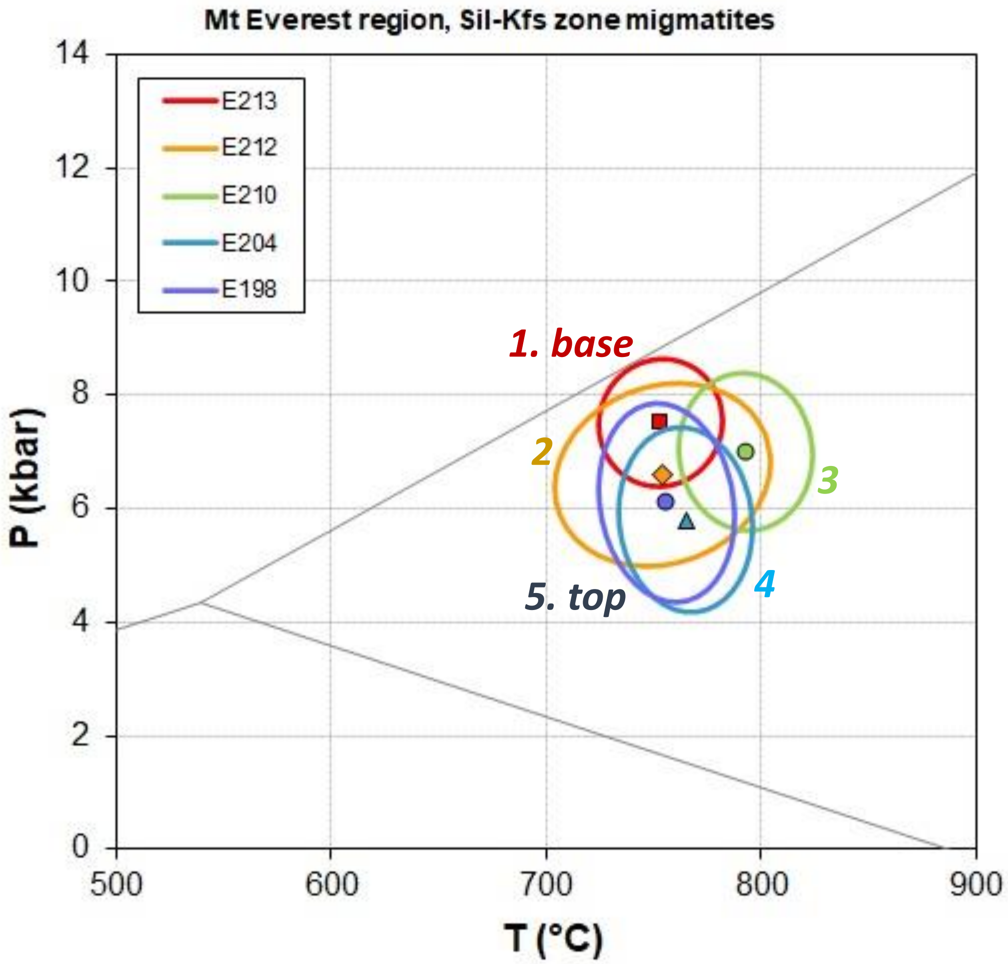


Relative uncertainty in average *P-T* calculations – examples

Uncertainty on end member activities only. Muscovite-bearing Ky/Sil mica schists, calculated assemblage Grt-Bt-Ms-Pl-Qz



Uncertainty on end member activities only. Migmatitic gneisses at higher structural level, assemblage Grt-Bt-Pl-Sil-Kfs-Qz



Estimating activities for multi-equilibrium thermobarometry

Generate your own (e.g. with TJB Holland's AX program)

Example AX output for typical Himalayan biotite:

```
Oxide     wt % cations   sd      activity   sd       %
SiO2     35.36  2.694  0.027    phl  0.036  0.00722  20
TiO2      2.37  0.136  0.005    ann  0.053  0.0093   18
Al2O3    19.58  1.759  0.028   east  0.039  0.0076   20
Cr2O3     0.00    -      -
Fe2O3     0.00    -      -
FeO      20.05  1.278  0.023
MnO       0.05  0.003  0.003
MgO       8.95  1.016  0.021
CaO       0.00    -      -
Na2O      0.22  0.033  0.008
K2O       7.99  0.777  0.018
Totals   94.57  7.696
```

Calculated for 11 oxygens.

Uncertainties on cations and on activities propagated from 0.05 wt% minimum plus 1.5% relative for each oxide.

Fe^{3+} from Tet + Oct cation sum = 6.9. Max ratio = 0.15

Solution model is Powell & Holland (1999, Am Min, 84, 1-14)

Fit your analyses to the 2014 solution model parameters

Biotite: $K[Fe^{2+},Mg,Mn]_2[Fe^{2+},Mg,Mn,Fe^{3+},Ti,Al][Al,Si]_2Si_2[OH,O]$

x(bi) = $Fe^{2+}/(Fe^{2+} + Mg)$

y(bi) = X(Al) in M3 site

f(bi) = X(Fe^{3+}) in M3 site

t(bi) = X(Ti) in M3 site [also m(bi) = XMn on 3 sites]

Further constraints:

- All sites filled – no vacancies
- Interlayer site filled with K
- Remaining oct+tet cations = 7
- Ti accommodated by oxy-substitution (deprotonation)
- Al(vi) and Fe^{3+} accommodated by additional Al(iv)

Note that Si is not directly calculated in this scheme, and only Al(vi) is evaluated. Therefore, Si = 3 – y(bi) – f(bi), Al(iv) = 4 – Si

For a typical Himalayan biotite (cations per 11+Ti oxygens):

	EPMA	model
Si	2.73	2.32
Al	1.78	2.20

these do not match, cannot be optimised

Effect of solution-model uncertainty on activities

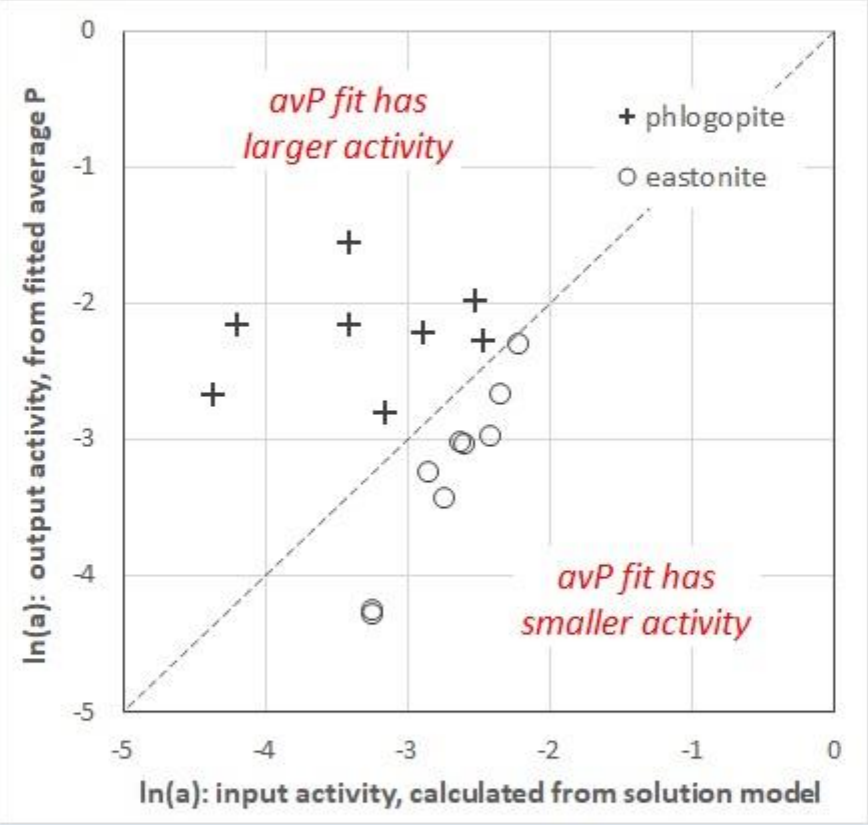
Detecting systematic uncertainty (bias) in solution models

Previous slide shows a potential source of systematic error in *P-T* calculations, arising from unintended consequences of harmless-looking solution model assumptions.

Here are input and output activities in biotite from average *P* calculations on nine varied amphibolite-facies rocks, calculated with HPds62 and the HPx-eos.

- The solution model increases the apparent Al(iv), decreases the apparent Si in biotite.
- Therefore, *compared to the EPMA mineral formula*,
  - the phlogopite activity is smaller than expected
  - The eastonite activity is larger than expected

The fit of the average P calculations is poor. The averaging process has shifted the output activities back towards values more like those expected from the EPMA formula recalculation!



Effect of solution-model uncertainty on activities

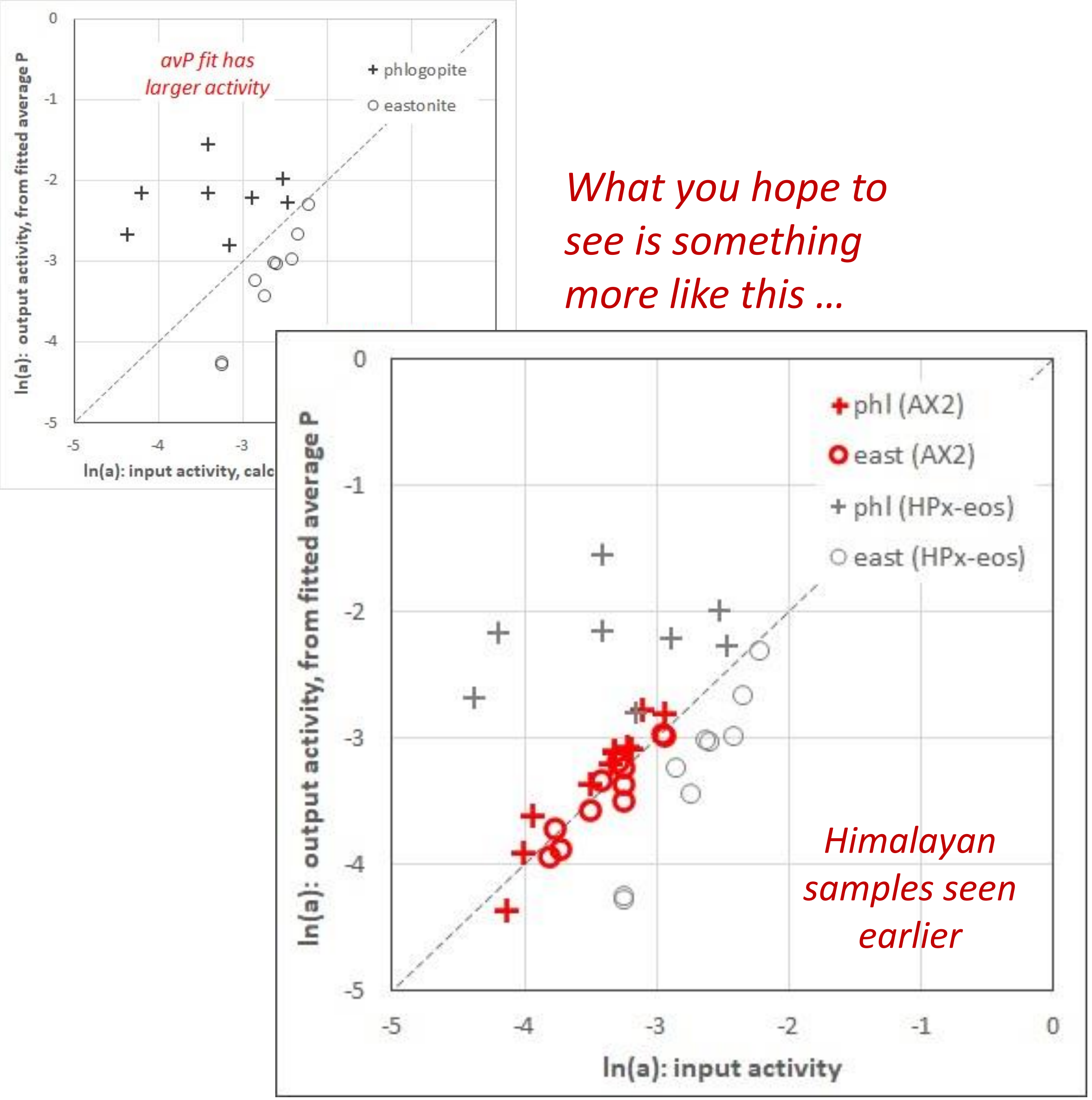
Detecting systematic uncertainty (bias) in solution models

Previous slide shows a potential source of systematic error in P-T calculations, arising from unintended consequences of harmless-looking solution model assumptions.

Here are input and output activities in biotite from average *P* calculations on nine varied amphibolite-facies rocks, calculated with HPds62 and the HPx-eos.

- The solution model increases the apparent Al(iv), decreases the apparent Si in biotite.
- Therefore, *compared to the EPMA mineral formula*,
  - the phlogopite activity is smaller than expected
  - The eastonite activity is larger than expected

The fit of the average P calculations is poor. The averaging process has shifted the output activities back towards values more like those expected from the EPMA formula recalculation!



What you hope to see is something more like this …

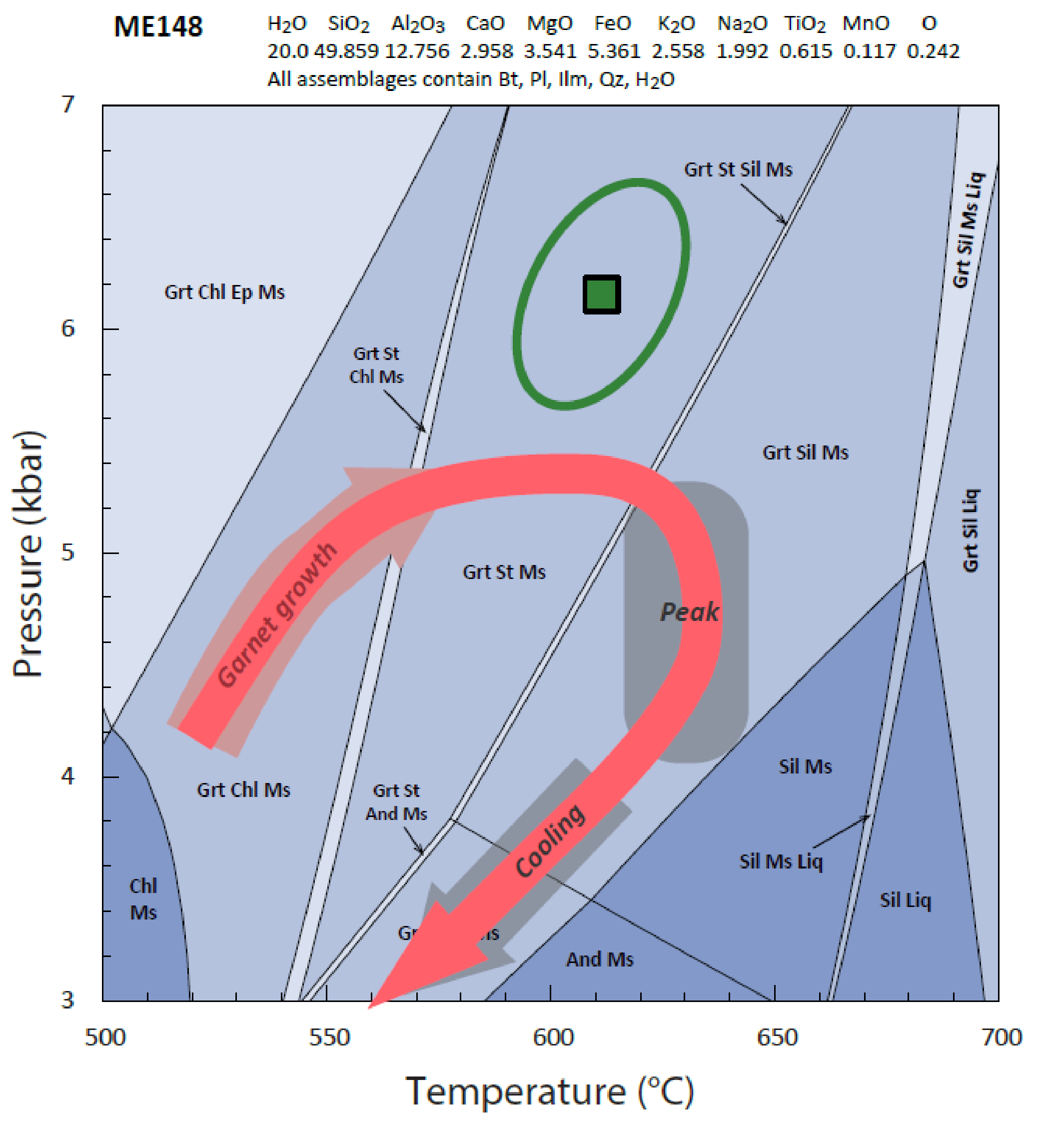
Himalayan samples seen earlier

Average *P-T* versus phase diagram

Average *P-T* works best with low-variance assemblages; but these may not be equilibrium associations.

ME148 Mt Everest metapelitic schist

- Full assemblage Grt-St-Sill-Bt-Ms-Pl-Qz-Ilm
- Assemblage theoretically stable in narrow field at first sillimanite isograd
- Average *P-T* gives a statistically acceptable result (green ellipse on figure) but is far removed from detailed path based on phase diagram, composition isopleths and detailed microstructures
- In this case, the principal clue is that there are no garnet compositions consistent with high-*T* conditions: all the garnet grew in the garnet zone, and it did not resorb and re-grow as predicted by equilibrium modelling

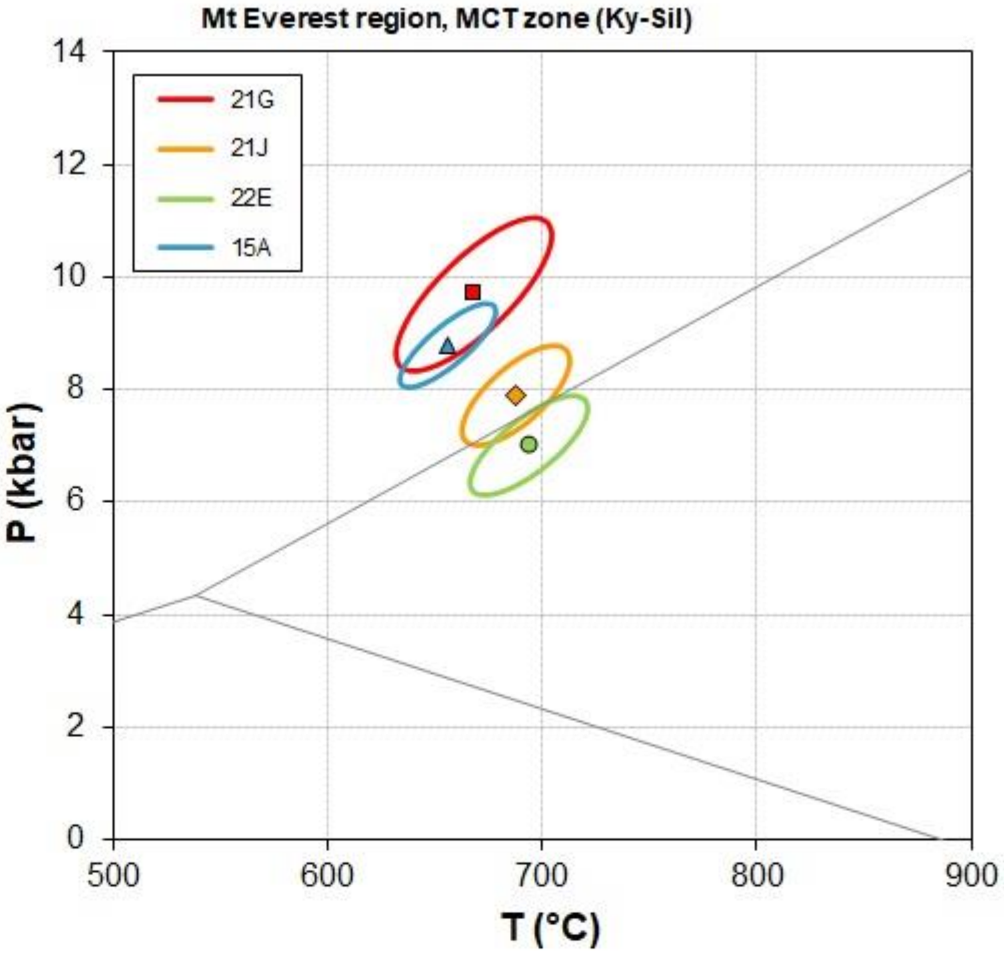


Overall (absolute) versus relative uncertainty

- What are our priorities in thermobarometry?
  - Depth in the crust, or thermal gradient (thermobaric ratio)?
    Needs absolute *P-T* constraints, i.e., accuracy as well as precision
  - Relative position or temperature difference between 2 or more samples?
    Needs precision but not necessarily accuracy.
    If using the same set of equilibria, dataset uncertainties can be largely eliminated

Apologies – have not considered high-pressure systems
Eclogite facies rocks: a complex topic, with problems including:

- Large high-variance fields e.g. with Grt, Na-Cpx, ±amphibole, show relatively little phase composition variation
- Consequently, large uncertainty on calculated *P-T*
- Issues with poorly constrained parameters, e.g. Fe^{3+} in Cpx etc



Best Practices in phase equilibrium modelling

- Choice of chemical system
- Approaches to bulk composition determination
- Checking calculated results
- Which features to monitor? Assemblage fields, isopleths, modes
- Isopleths for monitoring garnet growth
- Treatment of fluid composition or water activity
- Simple treatment of melt-bearing systems
- Final thoughts

Choice of system complexity

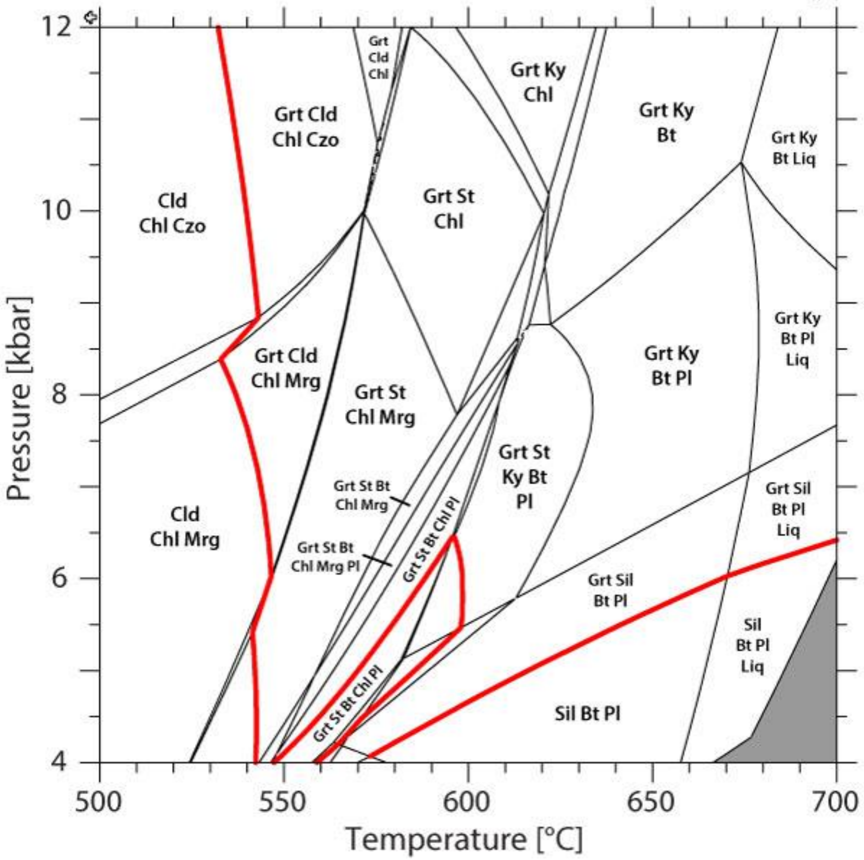
What system to choose? KFMASH; NCKFMASH; MnNCKFMASH; MnNCKFMASHTO?

Example from recent reviewing work – simple or complex system? I found adding Ti+O made a significant difference:

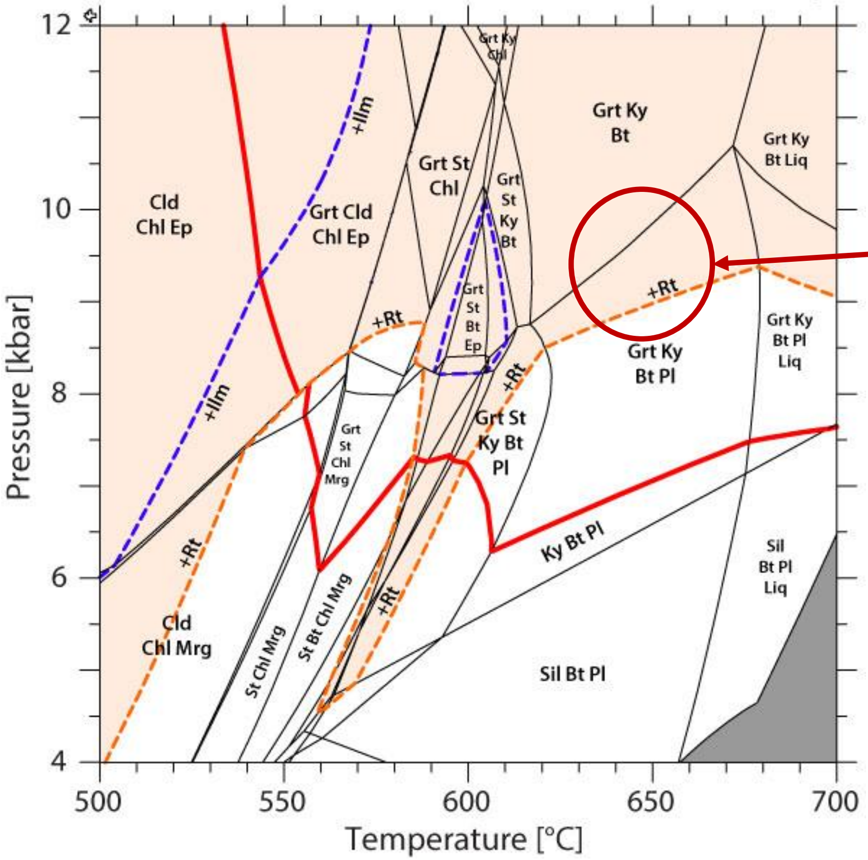
Discrepancy between phase diagram pressure (7–8 kbar) and independent P estimate (~11 kbar) at 600–650°C.

Rock contained ilmenite as the only Ti phase. MnNCKFMASHTO diagram confirms that phase diagram conditions are OK

MnNCKFMASH



MnNCKFMASHTO



This is the phase diagram manifestation of the GRAIL geobarometer – coexistence of rutile and ilmenite with garnet and kyanite

Note also the surprising effect on the stability field of garnet of adding ilmenite (and a tiny amount of Fe_2O_3) to the bulk composition

Bulk composition

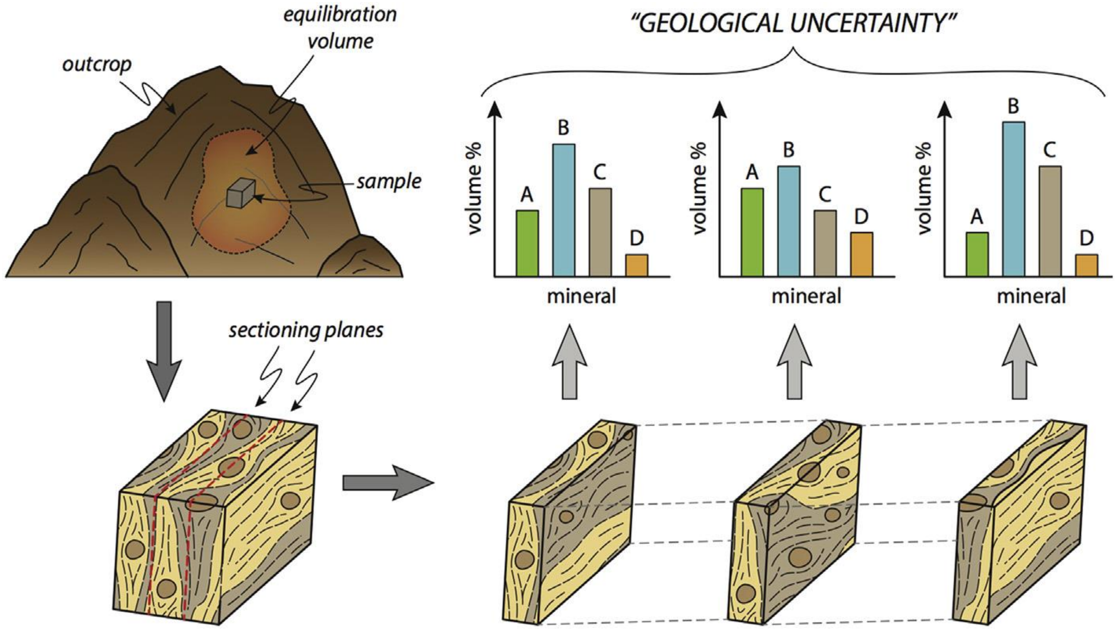
Methods for determining as summarized in Waters (2019) …

- XRF or other bulk destructive method (e.g. ICP-MS) on a separate part of the sample – may not be compositionally equivalent to the slide used for microprobe analysis.
- XRF etc. as above but on remainder of thin section rock billet (small sample, but closer approximation to composition of probe slide)
- Summation of mean EPMA analyses of major minerals combined with analysis of modal proportions.
  Care needed with zoned minerals. Be aware of solution model constraints – the 'ideal analysis' (P&H08) concept applies.
- Scanning the polished thin section area with SEM-EDS, EPMA or micro-XRF

Bulk methods are more problematic to correct for minor/accessory phases, cores of refractory minerals, etc.; strategies involving modal summation or scanning with spatial imaging are more readily adapted.

More to come later from Pierre Lanari

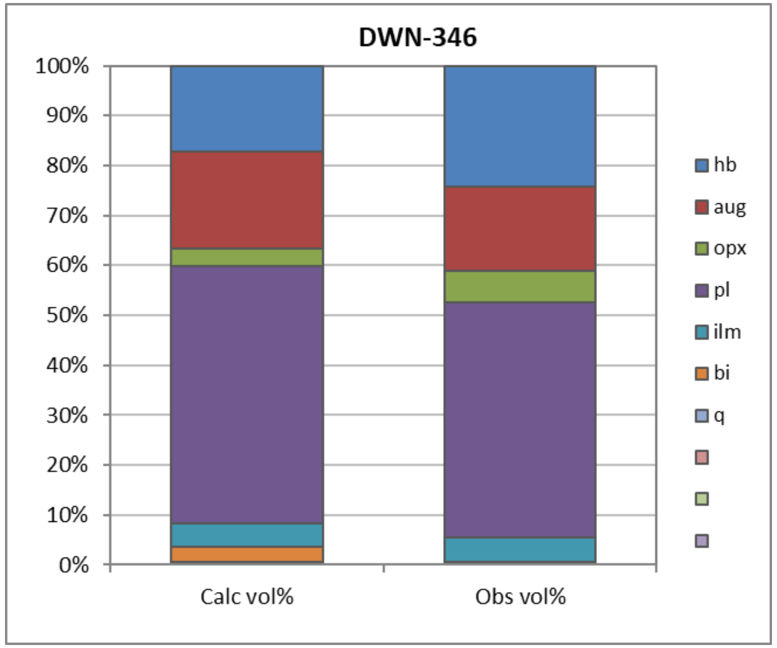
A reminder of 'Geological uncertainty' …

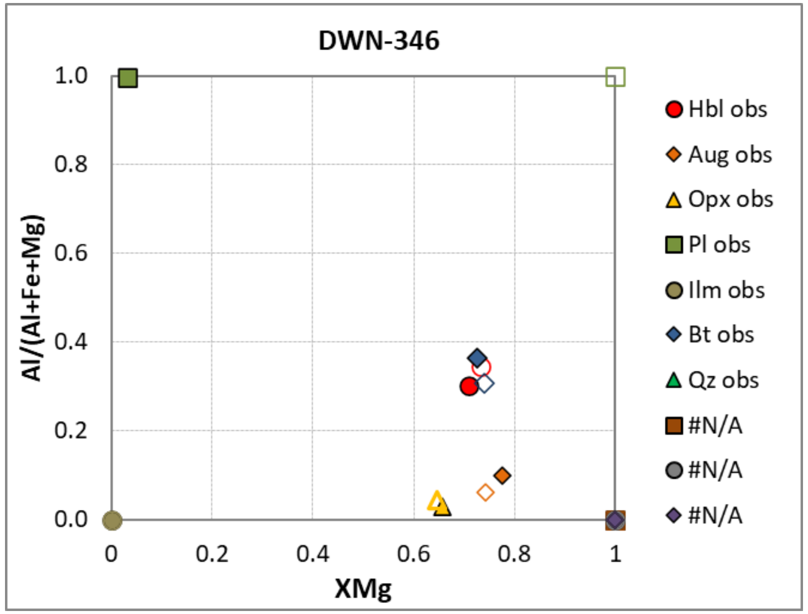


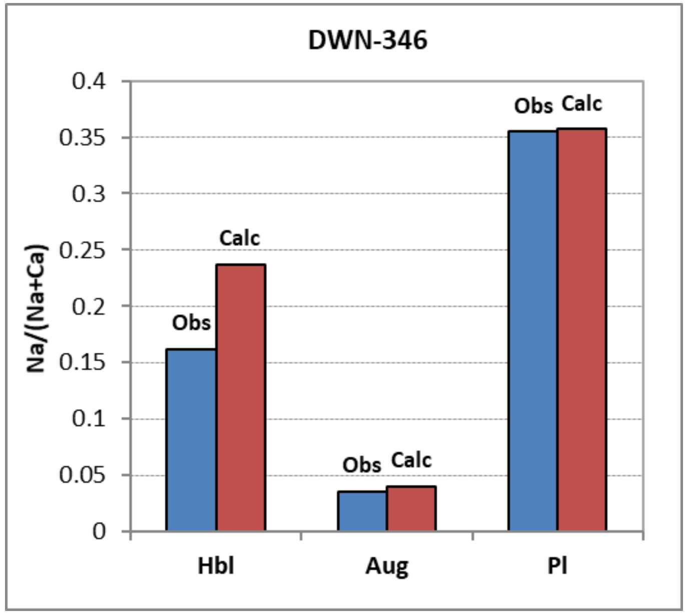
Checking calculated results: compositions and modes

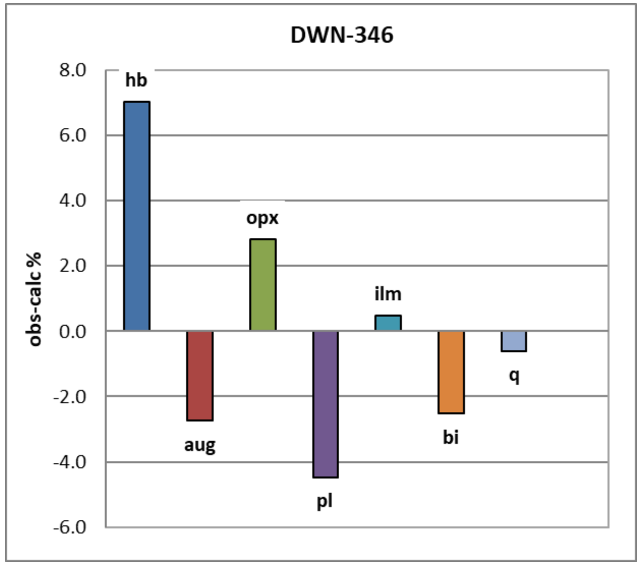
Graphical methods help to compare calculated results to the mineral compositions and modes in the modelled sample. How good is the match?

Our local semi-automated methods for THERMOCALC output use the ‘rbi’ matrix to plot these diagrams in MS-Excel







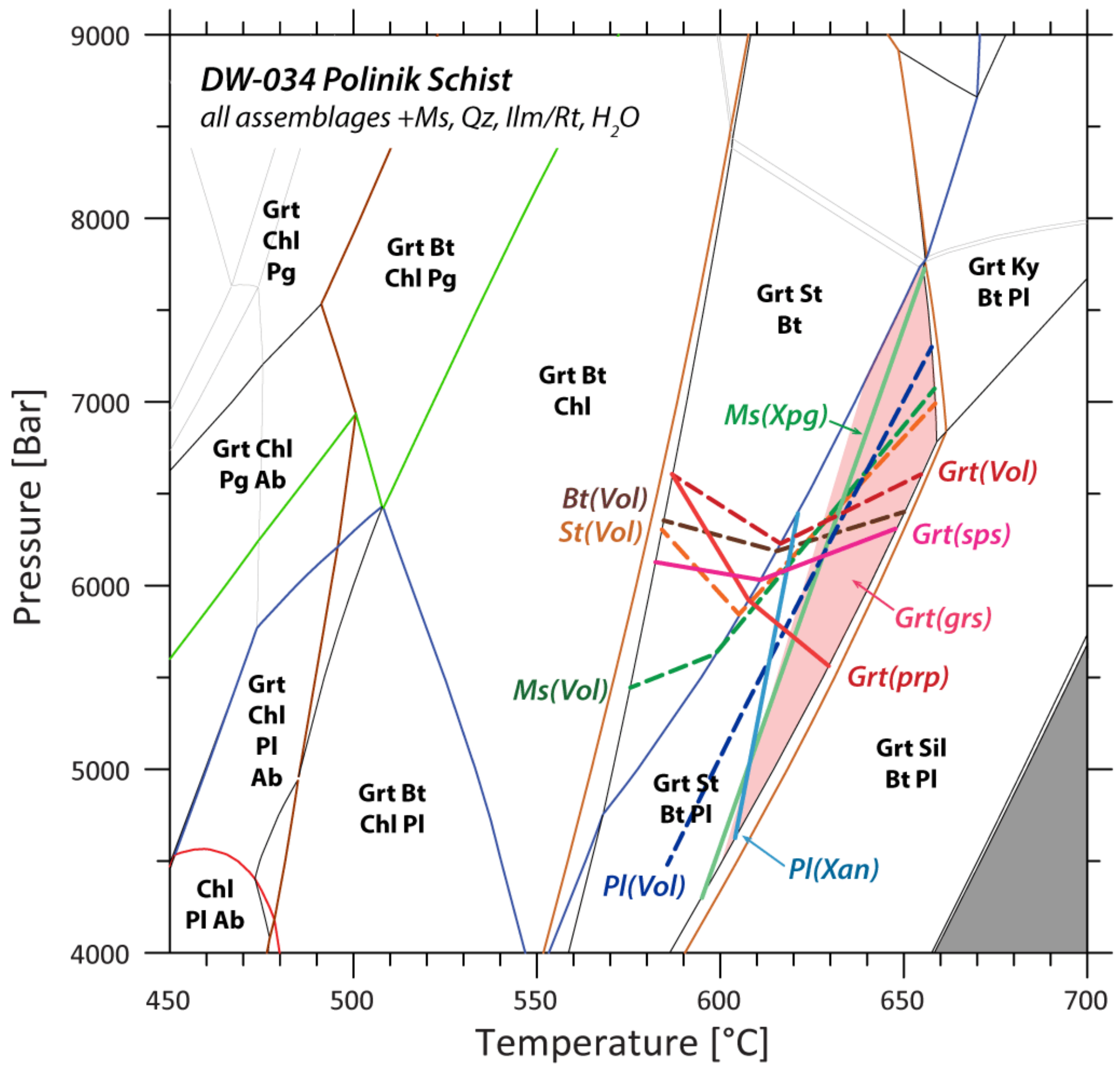


Data from a sample used in Forshaw et al. 2019, J metamorphic Geol

What to monitor

- Isopleths – argued earlier that these were generally the best choices; but be cautious in high-T rocks
    - Always check calculated phase compositions against observed minerals
- Modes – when are these most useful?
  Consider these for granulites, whose assemblages and modes reflect net-transfer equilibria, while mineral compositions may have undergone retrograde cation exchange
- Beware and be suspicious of apparent low-variance assemblages in small fields (see earlier example).
  What is the probability that these are true equilibrated assemblages?

Intersection of composition and mode isopleths



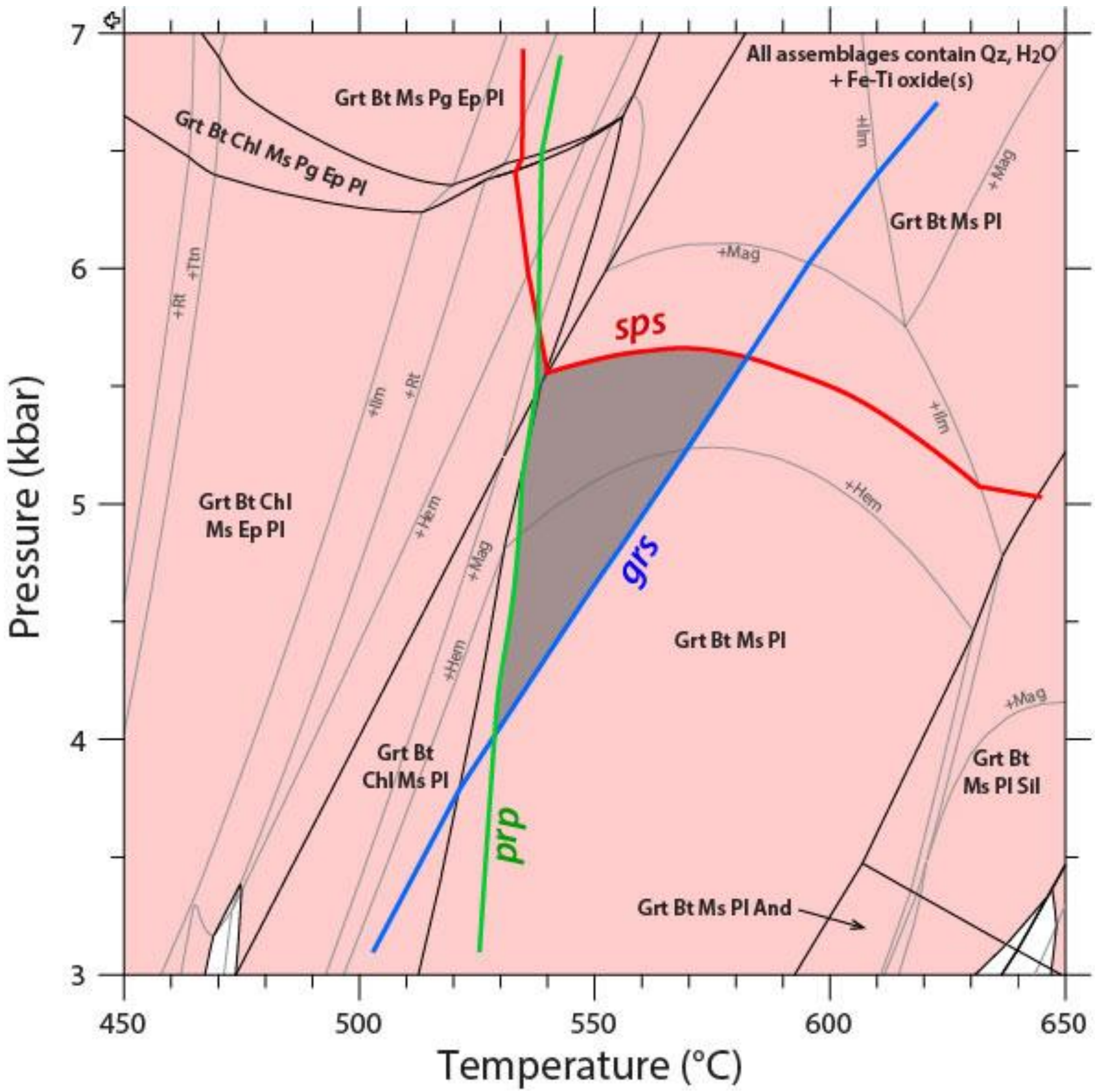
Isopleth intersections for monitoring garnet growth

- Mole fractions *alm prp grs sps*
  – can they be calculated – will they coincide?

- Which isopleths are most reliably constrained by precise equilibria?
  Answer: ***prp, grs***.
  However, with the HPx-eos, the pyrope isopleth cannot be directly calculated

- In this case note the poor coincidence of isopleths: unlike pyrope and grossular, the spessartine isopleth is sensitive to the balance of Mn in the system, suggesting there is a discrepancy between the observed and calculated modal proportions.

- What are suitable bulk compositions for monitoring garnet growth?
  'Average metapelite', with Na and Ca, is good.
  Low-Ca rocks, with no Pl, are problematic.



When isopleths do not intersect …

… there may be another good reason:

- Himalayan migmatitic Grt-Bt-Sil Kfs gneiss, showing tell-tale signs of retrograde Fe-Mg diffusional exchange.

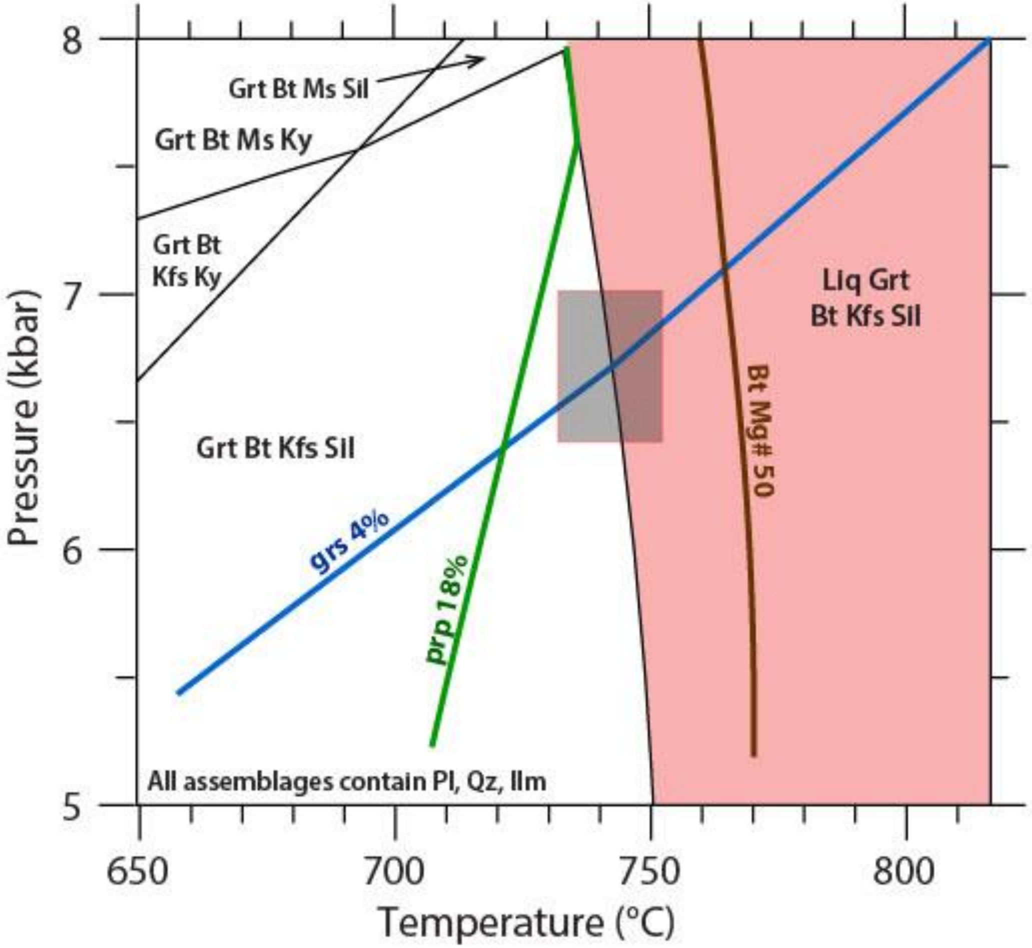
  Peak conditions taken to be at grey box, intersection of grossular garnet isopleth with the solidus.

  Isopleth for the pyrope content of garnet is displaced down-temperature: garnet contains less Mg than expected for peak 740°C

  Isopleth for the Mg content of biotite is displaced up-temperature: biotite is more Mg-rich than expected.

  This consistent with post-peak cation exchange.

  This is potentially a case where modal proportions could provide extra *P-T* control



H_2O contents

- Excess H_2O – when is this appropriate?

  A fair assumption for subsolidus systems dominated by hydrous phases

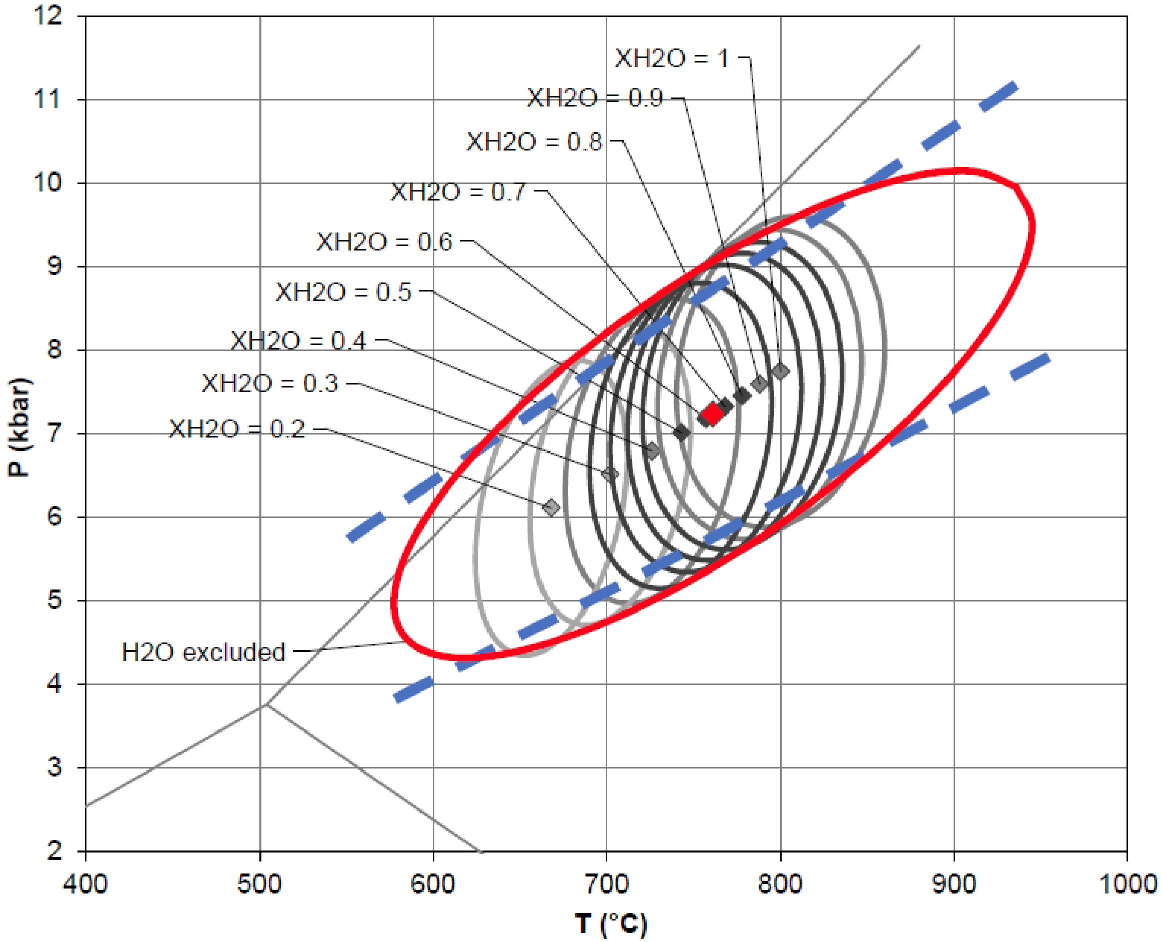
  For a phase diagram, choose bulk H_2O enough to saturate the most hydrous phase assemblage (usually near low-T, high-P corner)

- Graphitic systems – simplest approach in metapelites is to assume system is driven to maximum $X(H_2O)$ in mixed fluid by progressive dehydration ($X(H_2O)$ 0.7 to 0.9)

- Limits on H_2O content – how to estimate?
  - from hydrous mineral proportions
  - LOI from XRF sample determination (tricky)

- Fluid composition and water activity in average *P*-*T* thermobarometry

  – see diagram opposite …



- Grey ellipses: result for different values of $X(H_2O)$
- Red ellipse: calculation omitting H_2O
- Blue dashed lines: average-*P* envelope using same data
- These are one-sigma uncertainties!

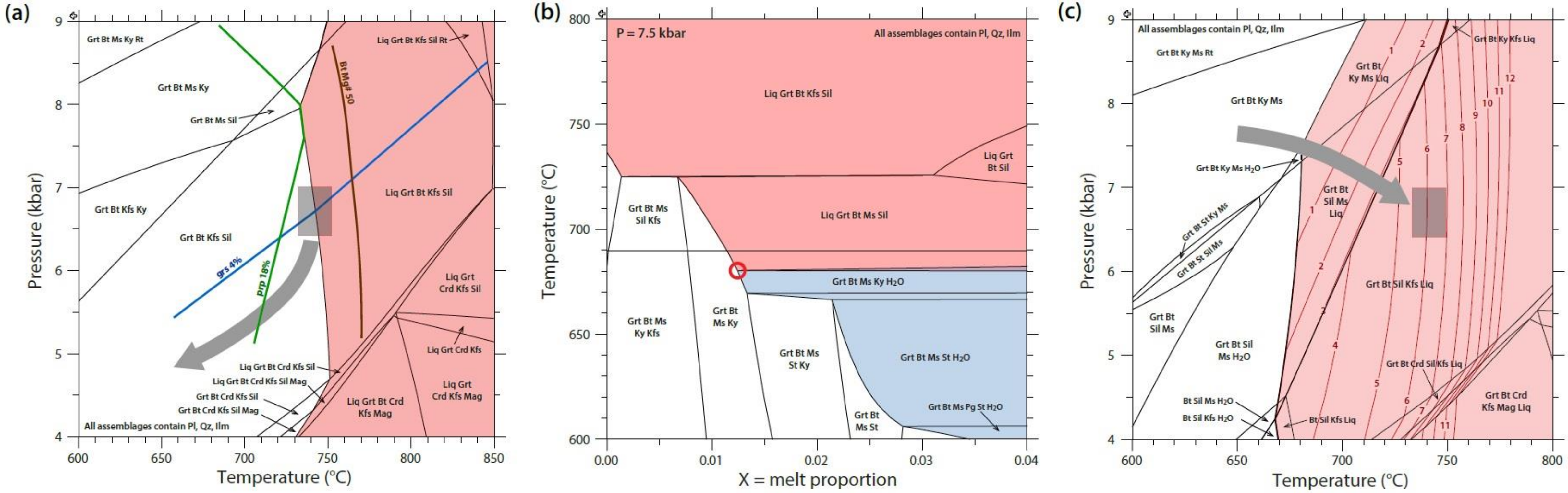
Melt-bearing systems

Himalayan example (Waters 2019), appropriate for migmatites that retain hydrous minerals …

a) Model the composition as now preserved. Diagram constrains peak condition at solidus (after melt loss). May be some clues as to later history.

b) Predicting or reconstructing the melting process: assume just H_2O-saturated at wet solidus, use T–X(melt) diagram to find T and amount of melt to re-integrate.

c) Calculate phase diagram for new bulk composition, define path from wet solidus to peak condition (contours are vol% melt)



Concluding comments

- Get to know the quirks of the dataset, solution models, and bulk compositions you are dealing with
- Always check calculated phase compositions against analyses from the natural sample
- Understand, and evaluate, if possible, the sources of uncertainty in your data and results: analytical imprecision; fundamental dataset uncertainty; solution model uncertainties; sampling bias (including ‘geological uncertainty’ on bulk composition and modal proportions)
- Rocks are not at fault if they don’t comply with equilibrium principles. We may be fortunate to find some that have approached homogeneous equilibrium, but departures from equilibrium tell us much about the evolution of the rock system

Some personal recommendations for clarity and uniformity in presentation of phase diagrams:

- Don’t clutter phase diagrams: generally, each one has a distinct purpose, so make sure the focus is obvious, and remove or fade out irrelevant or distracting detail.
- Use conventional abbreviations for phases and end members i.e. Whitney & Evans (2010) following Kretz (1983), rather than the non-standard ones used in particular packages.
  Capitalize the first letter for minerals, but use lower case for end members/phase components.

Bibliography and resources

- Forshaw JB, Waters DJ, Pattison DRM, Palin RM, Gopon P, 2019. A comparison of observed and thermodynamically predicted phase equilibria and mineral compositions in mafic granulites. *J metamorphic Geol,* 37 (2), 153-179
- Green ECR and others, 2020 onwards, *The HPx-eos and THERMOCALC*, https://hpxeosandthermocalc.org/
- Palin RM, Weller OM, Waters DJ, Dyck B, 2016. Quantifying geological uncertainty in metamorphic phase equilibria modelling; a Monte Carlo assessment and implications for tectonic interpretations, *Geoscience Frontiers*, 7 (4), 591-607.
- Powell R & Holland TJB, 1988, An internally consistent dataset with uncertainties and correlations: 3. Applications to geobarometry, worked examples and a computer program. *J metamorphic Geol*, 6, 173-204.
- Powell R & Holland TJB, 1993, The applicability of least squares in the extraction of thermodynamic data from experimentally bracketed mineral equilibria. *American Mineralogist*, 78, 107-112.
- Powell R & Holland TJB, 1994, Optimal geothermometry and geobarometry. *American Mineralogist*, 79, 120-133.
- Powell R & Holland TJB, 2006, *Course notes for "THERMOCALC Short Course" (Sao Paulo, Brazil)*, archived at https://serc.carleton.edu/research_education/equilibria/thermocalc.html
- Powell R & Holland TJB, 2008, On thermobarometry, *J metamorphic Geol*, 26, 155-179.
- Spear FS, 1993, *Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*, Mineralogical Society of America.
- Waters DJ, 1996–2004, *Practical aspects of mineral thermobarometry*, http://www.earth.ox.ac.uk/~davewa/pt/
- Waters DJ, 2019, Metamorphic constraints on the tectonic evolution of the High Himalaya in Nepal: the art of the possible, *Geol Soc London, Special Publications*, 483, 325-375.
- Worley B, Powell R, 2000, High-precision relative thermobarometry: theory and a worked example. *J metamorphic Geol*, 18, 91-101