thermobarometry

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- some overlap with my brasilia keynote...
- ...but hopefully covered at a slower pace!

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- single reaction ("directly-calibrated")
- multiple reaction (based on an internally-consistent dataset)
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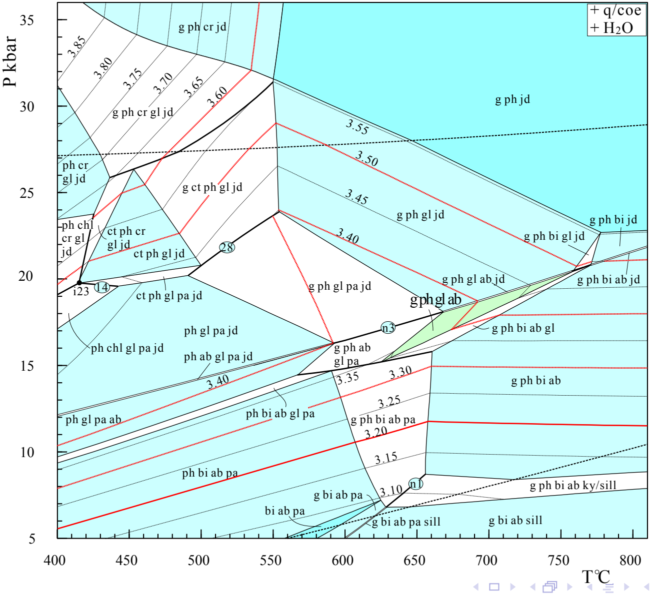
- calculated pseudosections
  - a powerful sort of thermobarometry, via
  - mineral stability fields
  - mineral proportion isopleths
  - mineral composition isopleths

pseudosection approach

- we have had a go at the pseudosection sort of thermobarometry, at least indirectly via learning how to calculate them

a garnet-glaucophane schist from the Tienshan



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- we have covered pseudosections at some length,
- so what I want to do is look at single- and multiple-reaction methods, particularly average PT, or $\overline{PT}$
  - acknowledging that single reaction methods should really be considered to be a subset of these
- in particular I want to look at
  - sources of uncertainty (in the context of the under-reporting of uncertainties in single-reaction thermobarometry),
  - and making all the methods, including pseudosections, thermodynamically consistent with each other

background

- conventional thermobarometry has tended to involve one or two equilibria, “directly-calibrated” from experimental and other data (e.g. g-bi Fe-Mg exchange thermometry combined with GASP)

- thermobarometry in an internally-consistent thermodynamic dataset setting (i.e. with those data having been through a thermodynamic “filter”) for example $\overline{PT}$

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- thermobarometry in an internally-consistent thermodynamic dataset setting (i.e. with those data having been through a thermodynamic "filter") for example $\overline{PT}$
  - merit of consistency with other mineral equilibria methods
  - possibility of realistic assignment of uncertainties, and so
  - possibility of recognising when there is little or no thermobarometric in a mineral assemblage

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- address the apparent disconnect between reported uncertainties on PT in this, and those implied by $\overline{PT}$
- I'll do this by looking at sources of uncertainty in general,
- then look at the g-cpx Fe-Mg exchange thermometer as an example.

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- *essential* idea in thermobarometry:
  - the **extrapolation** of experimental data on mineral properties and mineral equilibria in P, T and composition

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  - the **extrapolation** of experimental data on mineral properties and mineral equilibria in P, T and composition
- theme:
  - use equilibrium thermodynamics, as well as statistics, in order to do this. And common sense!

what is involved in thermobarometry? (2)

- formulation

- calibration

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  - realistic assessment/assignment of uncertainties .

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an aim is to calculate appropriate uncertainties on calculated PT values. How do the uncertainties arise? First:

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uncertainty in thermobarometry (3)

summarising, for PT calculations

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uncertainty in thermobarometry (4)

- sources of uncertainty arise from all of
  - formulation
  - calibration
  - application

garnet-clinopyroxene geothermometry

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- uncertainties commonly under-reported ($\pm 30^{\circ}\mathrm{C}$!)

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- composition dependence not in an activity coefficient form
- assumption of no ferric iron in the experiments used to calibrate the thermometer (maybe grossly unfair!?)

g-cpx example

let's look at an example: Proyer *et al.* (2004, *Contributions to Mineralogy and Petrology*, **147**, 305–318) for a Dabie Shan coesite-bearing eclogite (SM93).

This example is also used in an accompanying prac. Why? Because they have done Mössbauer on their minerals so they *know* how much ferric iron they have.

In a lot of conventional thermobarometry ferric iron is a major issue (because it is a critical unknown).

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  - mineral analysis uncertainty (1% relative on wt% oxides)
  - what to do about Fe^{3+}??
    charge balance calculation. . . (gives $\mathrm{Fe}^{3+} = 0$);
    or ignore it!! (is the same in this case)

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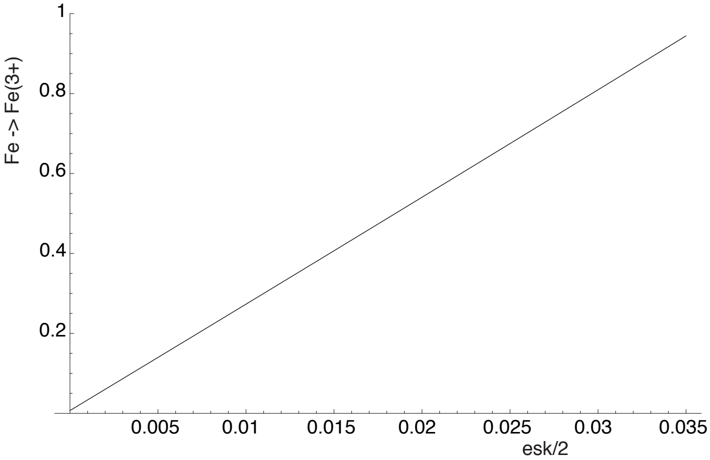
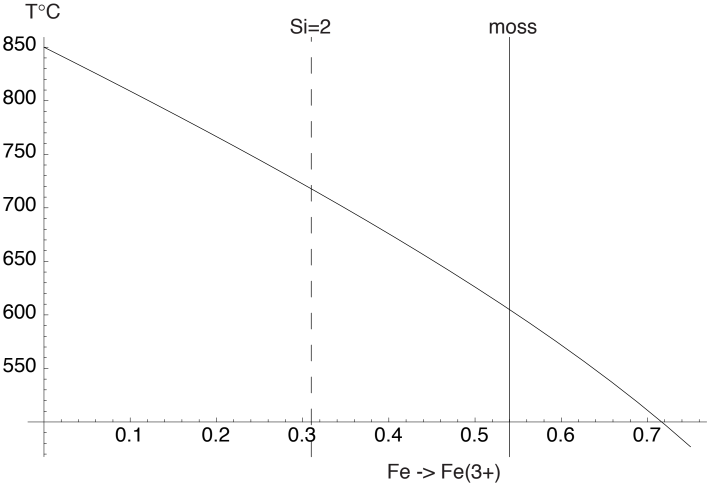
- but what charge balance calculation? What if there is significant Ca-eskola molecule in the cpx? (And what is significant?)
- alternatively, do a forward calculation, *specifying* Fe^{3+} (and Ca-eskola molecule) and calculating the "best" analysis (by least squares) corresponding to the specification.

effect of eskolaite



dependence of T on $\mathrm{FeO} \rightarrow \mathrm{Fe_2O_3}$ conversion (1)



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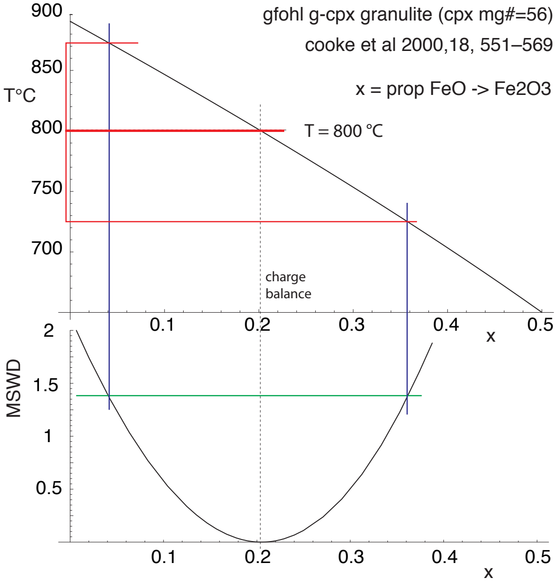
- Proyer *et al.* (2004), *determined* Fe^{3+}, so in that case uncertainties are reduced (do the prac to see the details)
- regularising calculations by using $\mathrm{Fe}^{3+} = 0$ is indefensible (because of the strong upwards bias on T)

dependence of T on $\mathrm{FeO} \rightarrow \mathrm{Fe_2O_3}$ conversion (2)



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- now let's say the calibration contribution to T uncertainty is $\sigma_T = 30^\circ$, with assumptions about the formulation and data
- so this is a minimum.

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- now let's say the calibration contribution to T uncertainty is $\sigma_T = 30^\circ$, with assumptions about the formulation and data
- so this is a minimum.
- the uncertainty on a temperature is therefore $2\sqrt{25^2 + 30^2}$, giving $T = 800 \pm 80^\circ\mathrm{C}$
- and this is certainly a minimum. . .

now to move on

- generalising, uncertainties in conventional thermobarometry *are* commonly under-reported

- let's now look at $\overline{PT}$

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  - possibility of realistic assignment of uncertainties (via the goodness of fit parameter involved)

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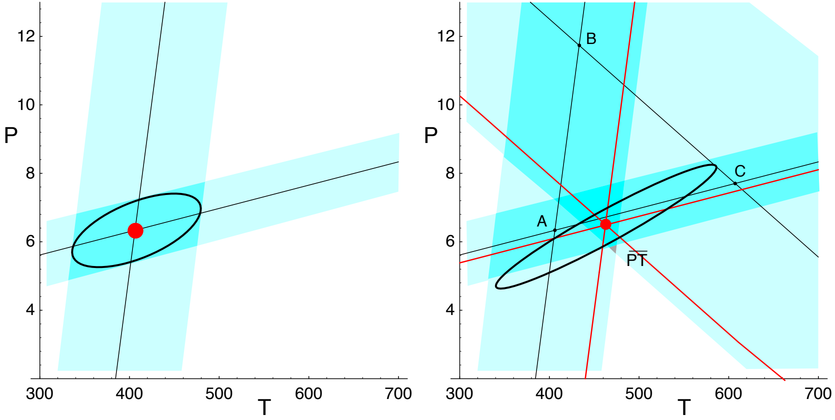
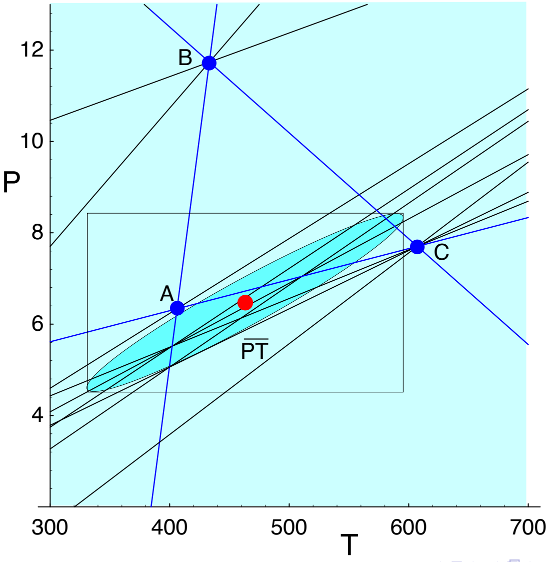
- then $\overline{PT}$ is the PT point that is as "close" as possible (in a least squares sense) to every reaction line

$\overline{PT}$ thermobarometry (1)



$\overline{PT}$ thermobarometry (2)



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- σ_{fit} depends on the size of the activity uncertainties: halving all the uncertainties, doubles the σ_{fit}.

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- is σ_{fit} minimised in T range? If so, try $\overline{PT}$

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- new way

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  - run mineral analyses through AX
  - assemble THERMOCALC datafile
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  - take mode 1 datafile *a*-*x* coding
  - convert recalculated analyses into $\{x, y, z \ldots\}$
  - run!

using mode 1 coding

- show example of the new way:
- Proyer's Dabie Shan rock

another $\overline{PT}$ example

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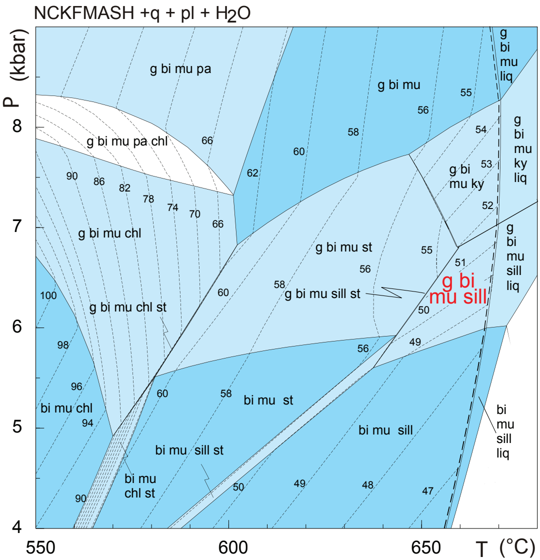
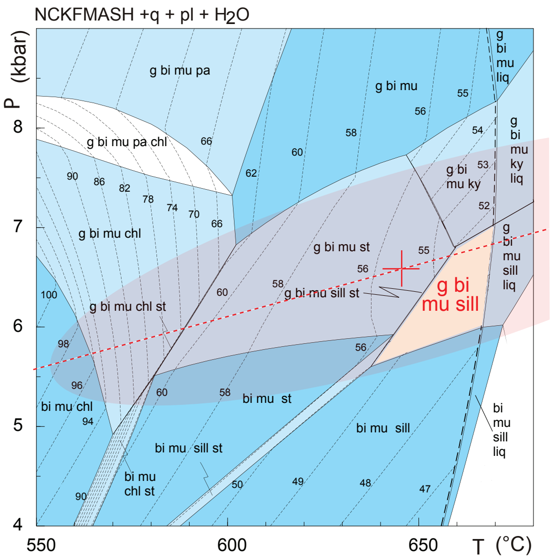
- we can see the shape of the phase relations using a PT pseudosection

the setting for a $\overline{PT}$ example



$\overline{PT}$ result



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  - therefore $\overline{PT}$ (and particularly $\overline{P}$) can certainly give thermobarometric information, at least on relatively low variance mineral assemblages,
  - and so locating these relatively low variance mineral assemblages, amongst the many mineral assemblages that you might have from an area, is important thermobarometrically
- but pseudosections are likely to provide the most powerful tools for thermobarometry (as I will argue at the Brasilia meeting coming up)