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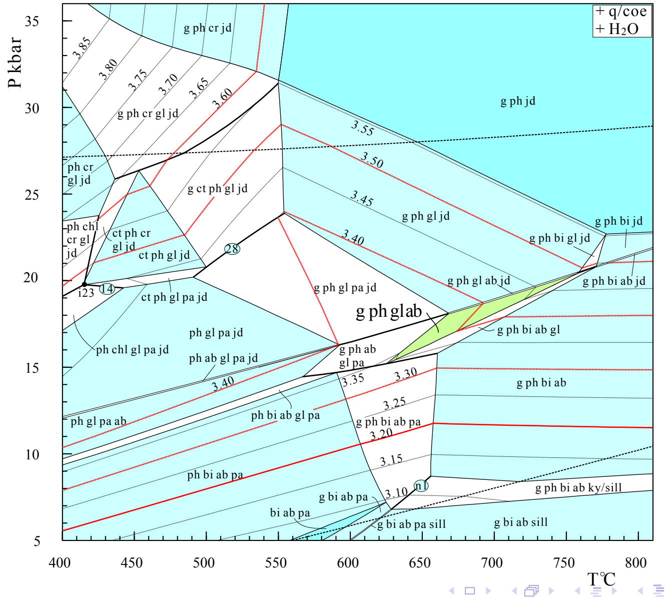
- calculated pseudosections
  - a powerful sort of thermobarometry, via
  - mineral stability fields
  - mineral proportion isopleths
  - mineral composition isopleths

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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  - 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 thermodynamically consistent with each other

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- 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)

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  - 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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- let's look at conventional thermobarometry, in general
- address the apparent disconnect between reported uncertainties on PT in this, and those impled 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.

what is involved in thermobarometry? (1)

- *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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uncertainty in thermobarometry (1)

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

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uncertainty in thermobarometry (4)

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

garnet-clinopyroxene geothermometry

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

recent calibration

The garnet–clinopyroxene Fe^{2+}–Mg geothermometer: an updated calibration

E. KROGH RAVNA
Department of Geology, University of Tromsø, N-9037 Tromsø, Norway (erlingr@ibg.uit.no)

ABSTRACT Multiple regression analysis on an extended dataset has been performed to refine the relationship between temperature, pressure, composition and the Fe–Mg distribution between garnet and clinopyroxene. In addition to a significant dependence between the distribution coefficient K_D and X_{Ca}^{Grt} and $X_{Mg\#}^{Grt}$, as shown by the experimental data, the effect of X_{Mn}^{Grt} has also been incorporated using data from natural Mn-rich garnet–clinopyroxene pairs. Multiple regression of data ($n = 360$) covering a large span in pressure, temperature and composition from 27 experimental datasets, combined with 49 natural high-Mn granulites from Ruby Range, Montana, USA, and Karnataka, India, yields the P–T–compositional relationship ($r^2 = 0.98$):

$$T(^\circ C) = [(1939.9 + 3270\ X_{Ca}^{Grt} - 1396\ (X_{Ca}^{Grt})^2 + 3319\ X_{Mn}^{Grt} - 3535\ (X_{Mn}^{Grt})^2 + 1105\ X_{Mg\#}^{Grt}$$
$$- 3561 (X_{Mg\#}^{Grt})^2 + 2324\ (X_{Mg\#}^{Grt})^3$$
$$+ 169.4\ P(\text{GPa}))/(\ln K_D + 1.223)] - 273$$

where $K_D = (Fe^{2+}/Mg)^{Grt}/(Fe^{2+}/Mg)^{Cpx}$, $X_{Ca}^{Grt} = Ca/(Ca + Mn + Fe^{2+} + Mg)$ in garnet, $X_{Mn}^{Grt} = Mn/(Ca + Mn + Fe^{2+} + Mg)$ in garnet, and $X_{Mg\#}^{Grt} = Mg/(Mg + Fe^{2+})$ in garnet. The Fe^{2+}–Mg equilibrium

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summarising problems (relating to using the Krogh Ravna equation for *extrapolation*—as is involved in nearly all thermometry)

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- not utilising all information available (ΔV and ΔS of the Fe-Mg exchange reaction)
- composition dependence not in an activity coefficient form
- assumption of no ferric iron in the experiments used to calibrate the thermometer (maybe grossly unfair!?)
- *but* it is the best g-cpx thermometer out there currently...

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).

Si	Al	Fe^{3+}	Fe^{2+}	Mg	Ca	Na
2.01554	0.48883	0	0.11303	0.41074	0.44315	0.52342

with minor Ti, Cr, Mn and K, not shown.

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)

mineral recalculation

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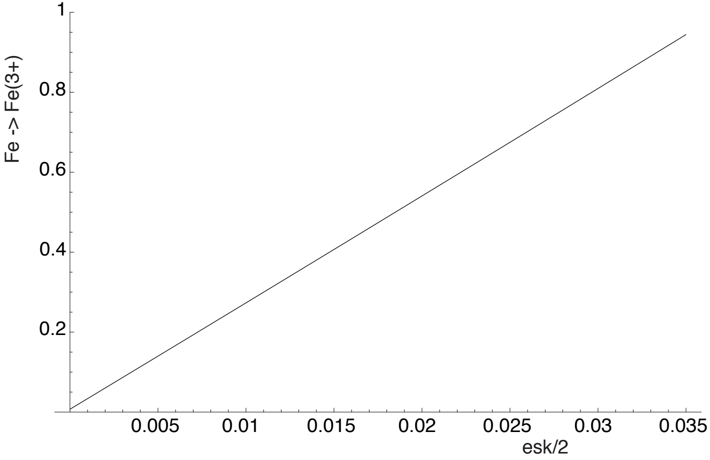
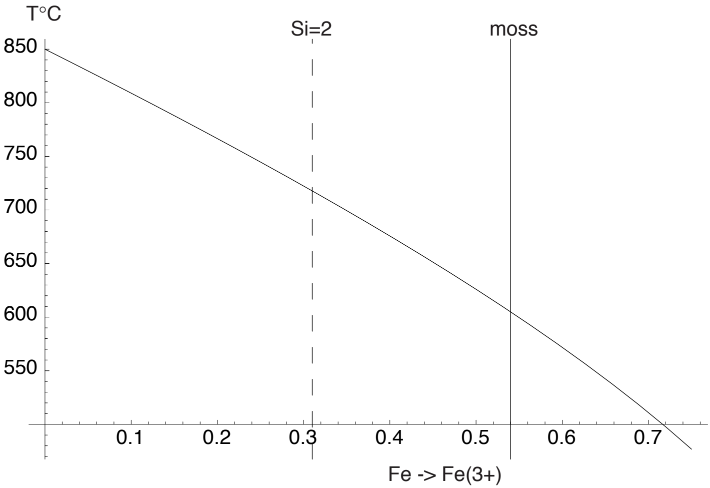
- alternatively, do a forward calculation, *specifying* Fe^{3+} (and eskolaite) and calculating the "best" analysis (by least squares) corresponding to the specification.

effect of eskolaite



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



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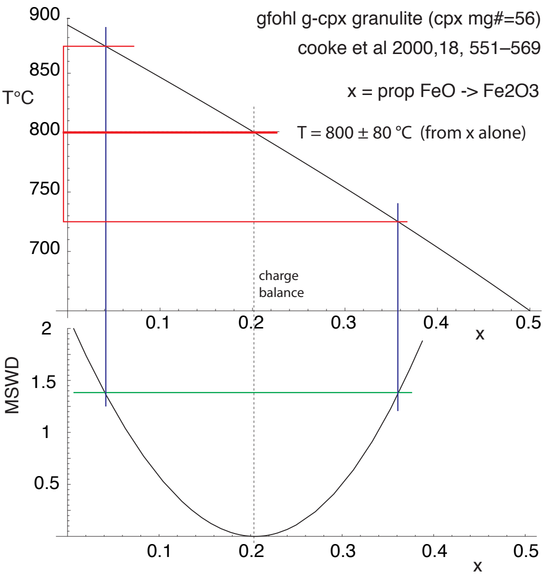
- uncertainties arising from unknown Fe^{3+} are huge
- Proyer *et al.* (2004), *determined* Fe^{3+}, so in that case uncertainties are reduced (do the prac to see the details)
- regularising calculations by using $\mathrm{Fe}^{3+} = 0$ is indefensible (because of the strong upwards bias on T)
- real implications for "maximum astonishment" publications: unfortunately doing the wrong thing with g-cpx thermometry is used to support what I think is a misidentification of peak metamorphic mineral assemblage...

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



dependence of T on $\mathrm{FeO} \rightarrow \mathrm{Fe_2O_3}$ conversion (3)

so let's estimate a T uncertainty for this cooke et al example

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- for $\mathrm{MSWD} < 1.5$, the T range around $800^\circ\mathrm{C}$ is $720^\circ < T < 880^\circ\mathrm{C}$
- error propagation approach gives $\sigma_T = 25^\circ$

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- the uncertainty on a temperature is therefore $2\sqrt{25^2 + 30^2}$, giving $T = 800 \pm 80°\mathrm{C}$
- and this is certainly a minimum...

now to move on

- generalising, uncertainties in conventional thermobarometry *are* commonly under-reported
- let's now look at $\overline{PT}$

average PT

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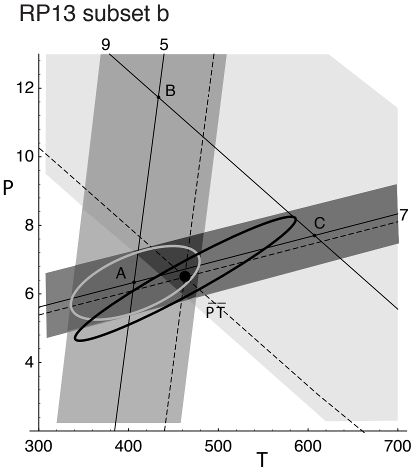
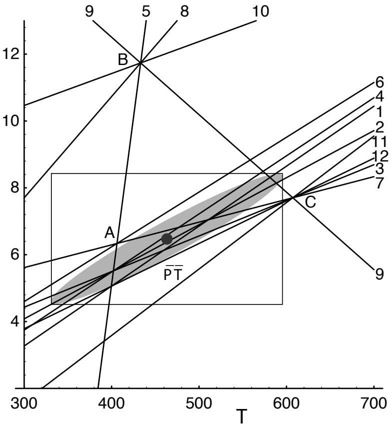
  - possibility of realistic assignment of uncertainties (via the goodness of fit parameter involved)

conventional and $\overline{PT}$ thermobarometry





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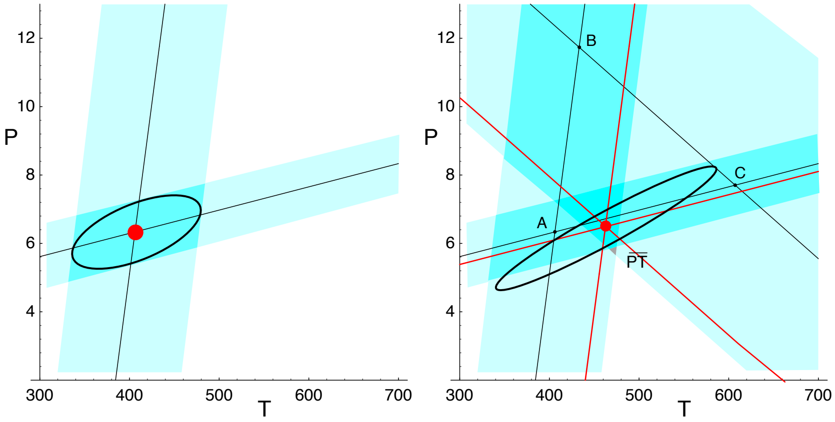
- then $\overline{PT}$ is the PT point that is as "close" as possible (in a least squares sense) to every reaction line

$\overline{PT}$ thermobarometry (1)



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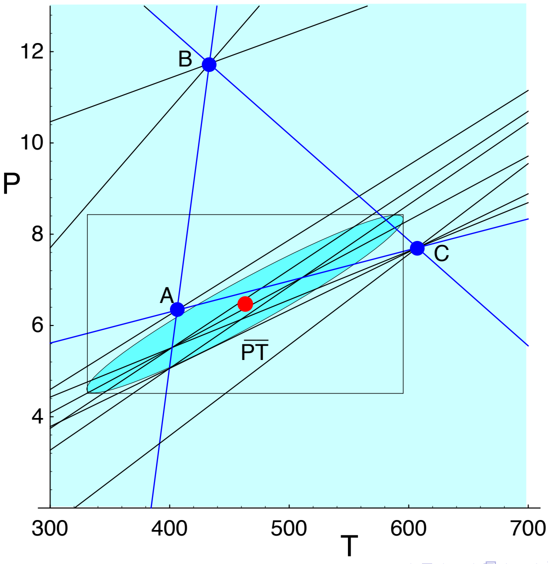

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- σ_{fit} depends on the size of the activity uncertainties: halving all the uncertainties, doubles the σ_{fit}.

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

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

an $\overline{PT}$ example

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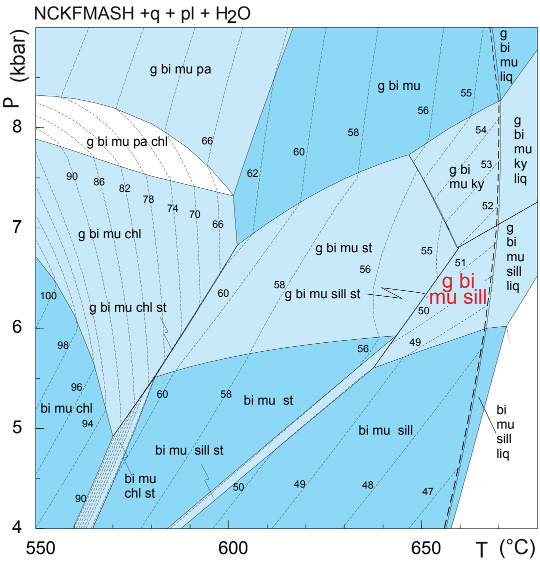
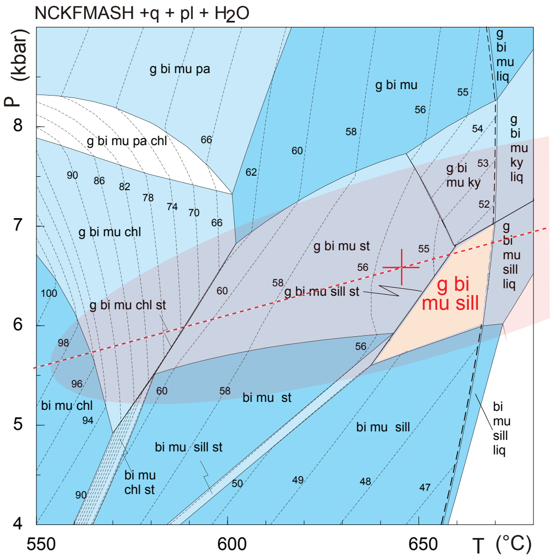
- we can see the shape of the phase relations using a PT pseudosection

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



$\overline{PT}$ result



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  - 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)