Day 2, Part I
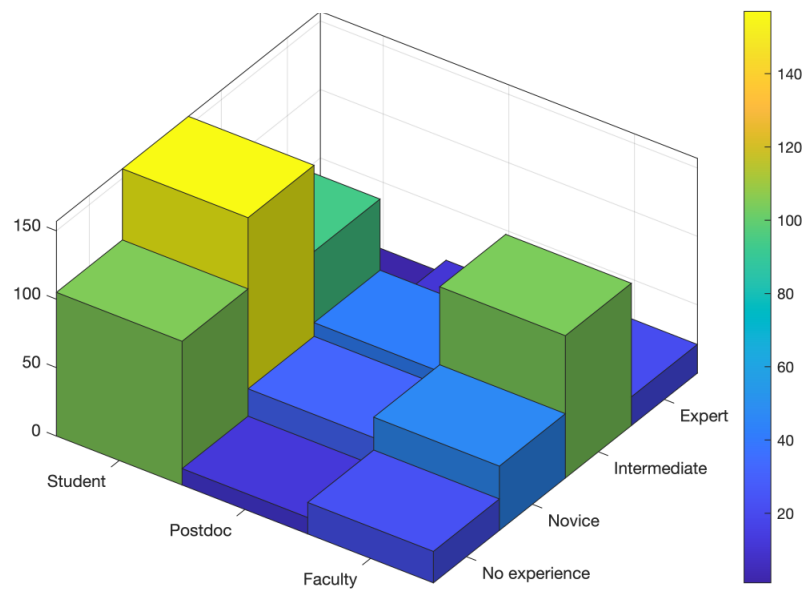# Perple_X: General Strategies, Strengths and Weaknesses
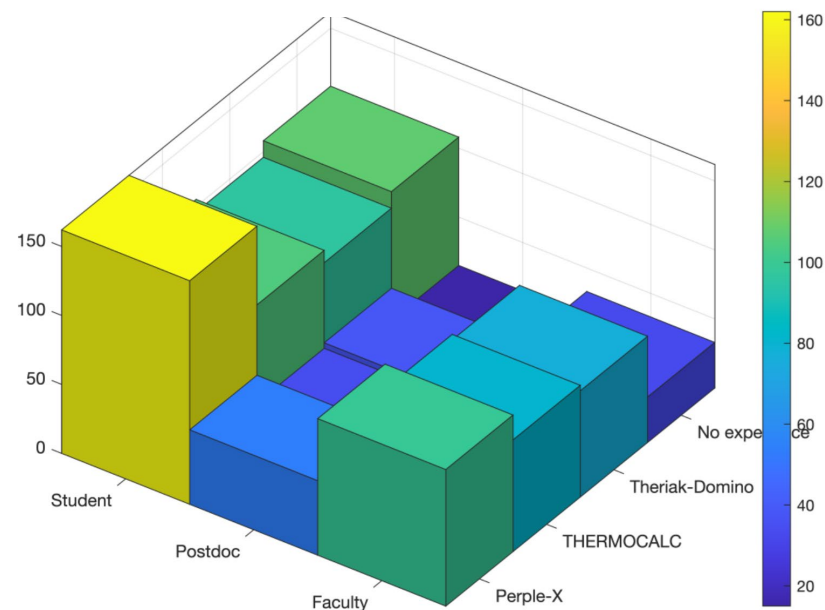
Mark Caddick, Virginia Tech

PHASE EQUILIBRIUM MODELLING: APPROACHES AND PITFALLS
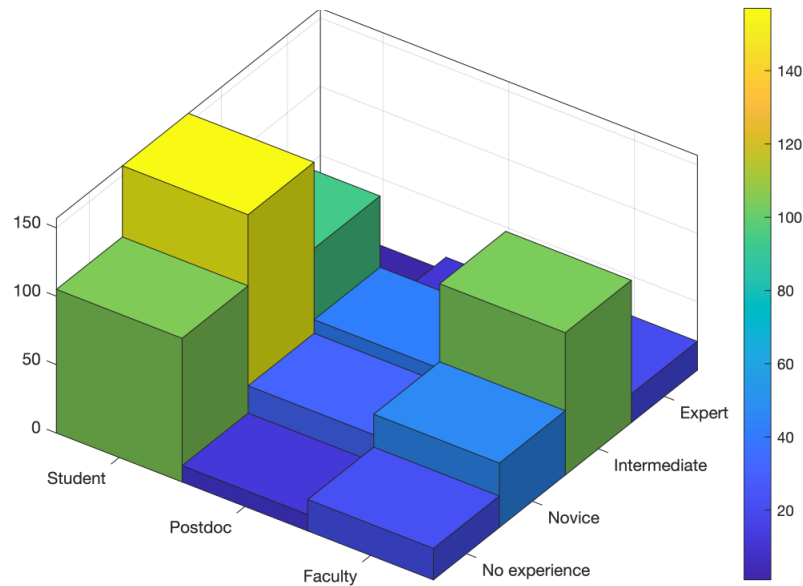
Experience with phase equilibrium modelling

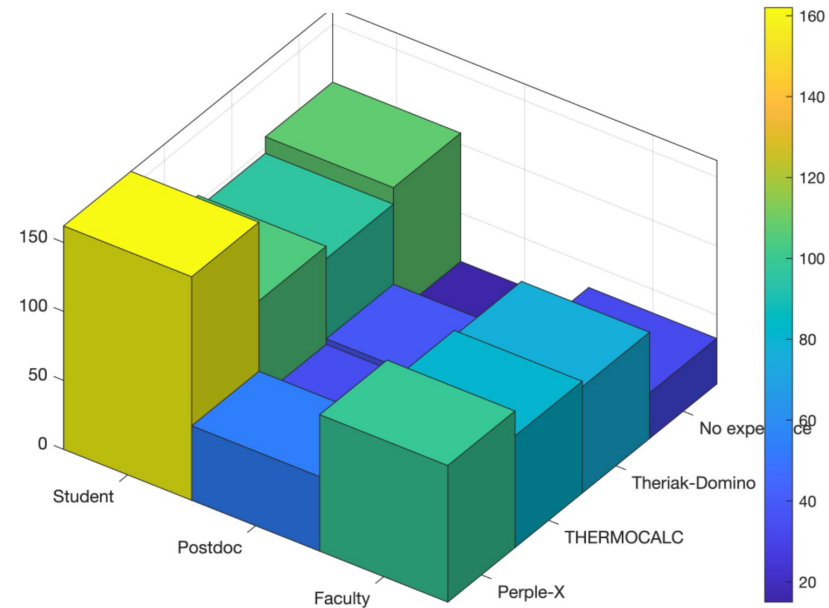Experience with phase equilibrium modelling software packages

What this talk will involve

- An overview of what Perple_X is and some of the things it can do
- A discussion of some of the strategies it employs
- An introduction to how calculations are structured

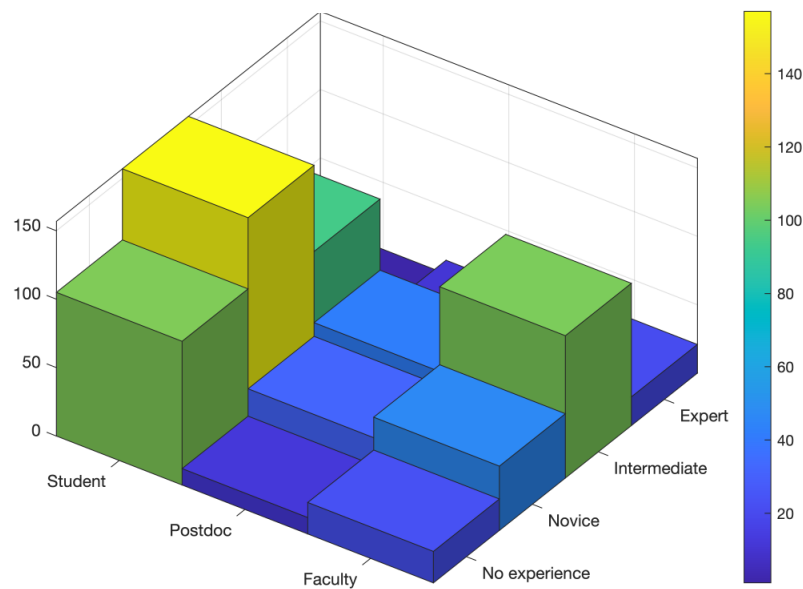Experience with phase equilibrium modelling

Experience with phase equilibrium modelling software packages

What this talk will not be

- A detailed 'how to' for any given problem in Perple_X
- An overview of all of the parameters required for a 'good' result
- A deep dive into everything that Perple_X can do and exactly how it does it

Experience with phase equilibrium modelling

Experience with phase equilibrium modelling software packages

What this talk will not be
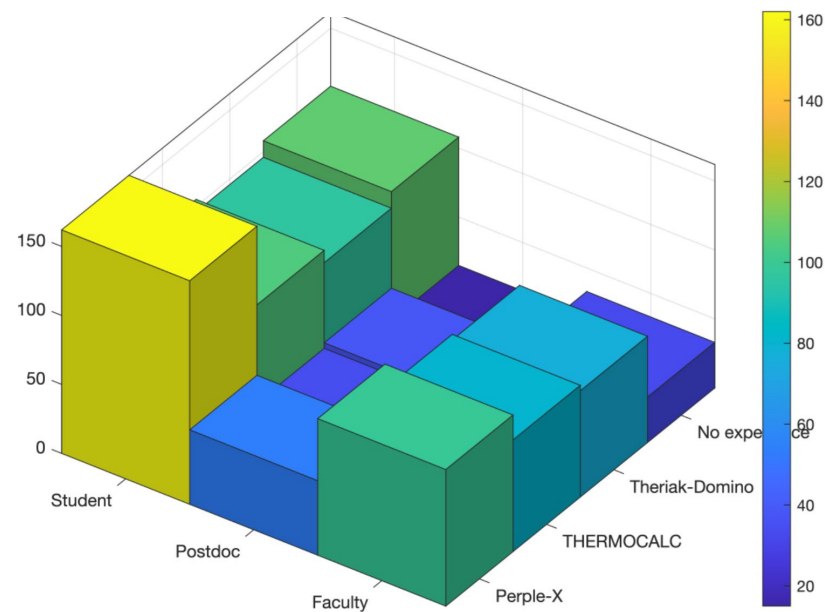
• A statement about whether Perple_X is better or worse than any other package

PHASE EQUILIBRIUM MODELLING:
APPROACHES AND PITFALLS

Key topics and objectives of the lecture

- What is Perple_X and where can I find it?

- How is Perple_X's strategy different to THERMOCALC's

- In practice, what does a calculation involve?

- What end-member and solid solution models are available?

- Can Perple_X replicate results calculated with THERMOCALC?

- Calculating phase abundances and compositions, and 'physical properties'

- Phase fractionation

- Strengths and weaknesses

- Additional reading

What is Perple_X?

PHASE EQUILIBRIUM MODELLING:
APPROACHES AND PITFALLS

- Perple_X is a modular set of command-line operated programs, which are available from here: http://www.perplex.ethz.ch

- That website also has links from which you can download thermodynamic data appropriately formatted for use in Perple_X

- There are also some tutorials, though they are mostly out of date because the code has evolved substantially in the last decade

- There is also a user group, that you can register for here: https://groups.io/g/PerpleX

- Perple_X is very flexible, calculating:

  - *PT* projections

  - Bulk-rock dependent phase diagrams

  - Compatibility diagrams

  - Mixed-variable diagrams

  - μ-μ diagrams

  - Diagrams in which one or several phases are progressively fractionated from the 'bulk-rock' composition

- Perple_X may be initially confusing because of the scope of what it can calculate.

- Perple_X is very flexible, calculating:

  - *PT* projections

  - Bulk-rock dependent phase diagrams

  - Compatibility diagrams

  - Mixed-variable diagrams

  - μ-μ diagrams

  - Diagrams in which one or several phases are progressively fractionated from the 'bulk-rock' composition

- Perple_X has been widely adopted by the geodynamics community (for reasons that will hopefully become clear soon)

- Perple_X is written and maintained by Jamie Connolly (ETH Zürich)

- Perple_X is written in FORTRAN. Source code is not available for open download

- The algorithm dates back to the late 1980s, but Perple_X has undergone substantial updates (particularly in the last 15 years)

Connolly, J.A.D., Kerrick, D.M., 1987. An algorithm and computer program for calculating composition phase diagrams. *Computers and Geosciences* **11**, 1-55.

Connolly, J.A.D., 1990. Multivariable phase diagrams: an algorithm based on generalized thermodynamics. *Am. J. Sci.* **290**, 666-718.

Kerrick, D.M., Connolly, J.A.D., 2001. Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. *Nature* **411**, 293-296.

Connolly, J.A.D., Petrini, K., 2002. An automated strategy for calculation of phase diagram sections and retrieval of rock properties as a function of physical conditions. *J. Metamorph. Geol.* **20**, 697-708.
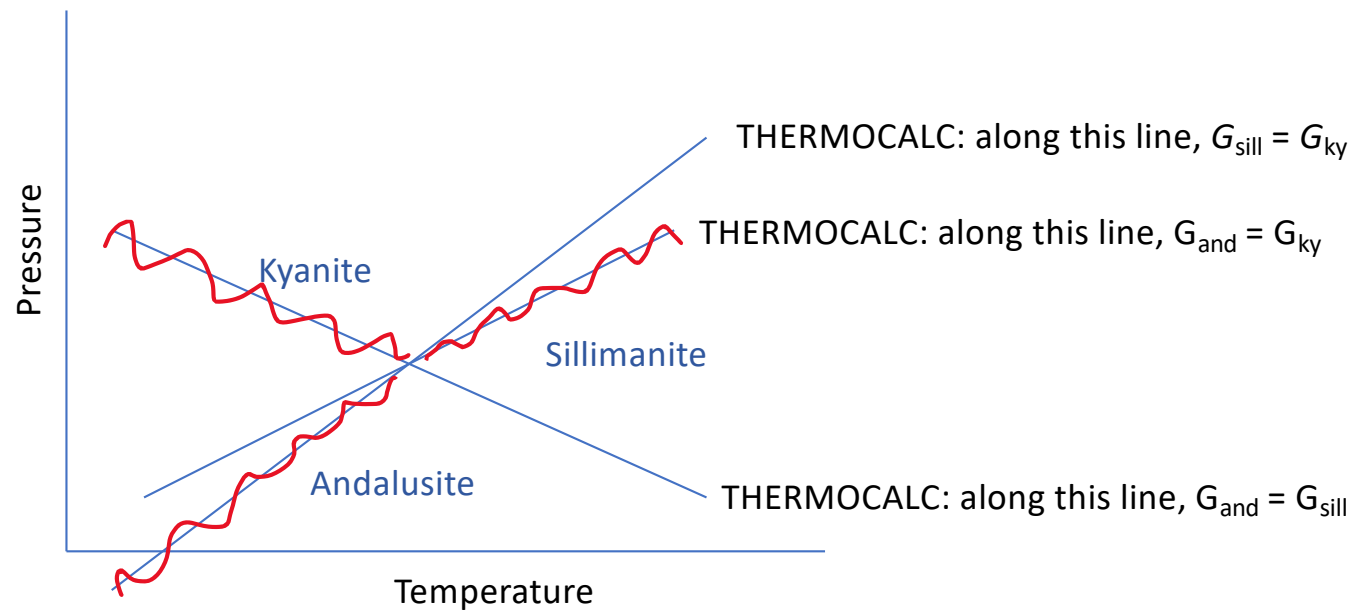
Connolly, J.A.D., 2005. Computation of phase equilibria by linear programming: A tool for geodynamic modeling and its application to subduction zone decarbonation. *Earth Planet. Sci. Lett.* **236**, 524-541.
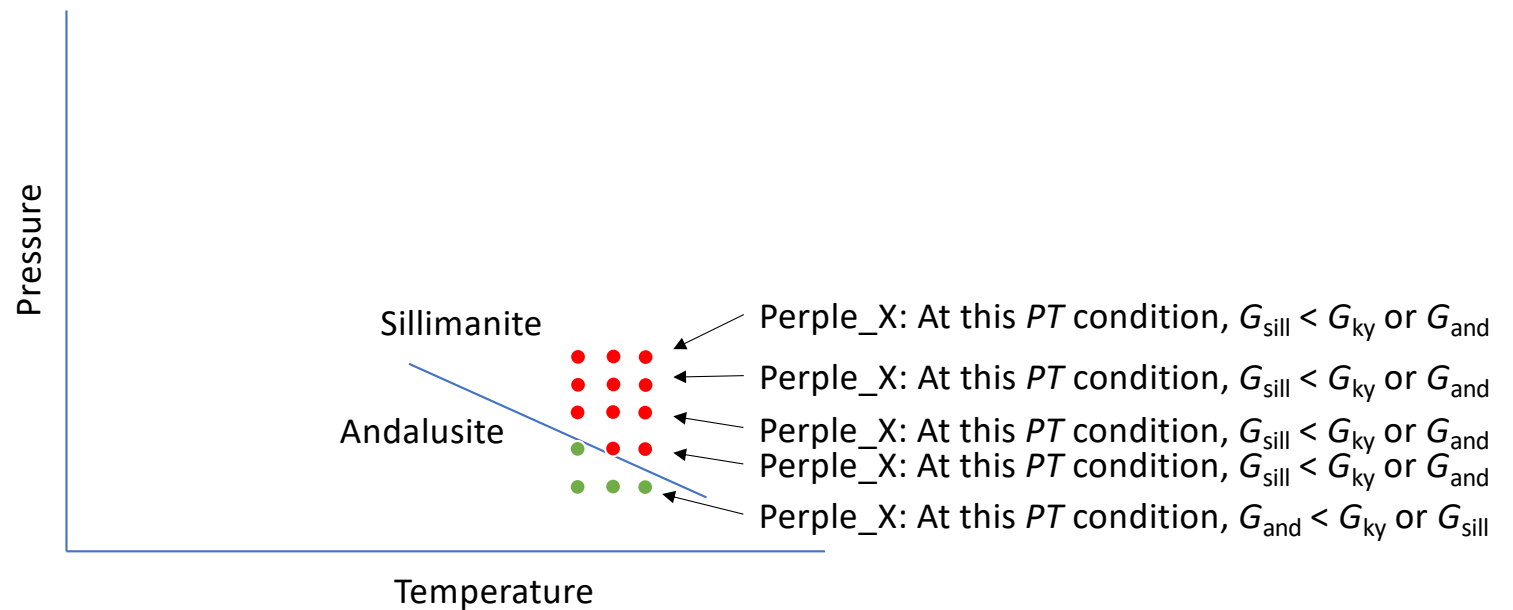
Connolly, J. A. D. & Galvez, M. E., 2018. Electrolytic fluid speciation by Gibbs energy minimization and implications for subduction zone mass transfer. *Earth and Planetary Science Letters*, **501**, 90-102.

How Does Perple_X Differ from THERMOCALC?

Perple_X calculates the configuration of phase identities, abundances and compositions that yields the lowest Gibbs free energy at a given *PT* condition. The user identifies the range of phases (minerals, melts, fluids) that Perple_X should consider and the program decides which subset of these is stable. This requires one absolutely critical assumption.

THERMOCALC finds the conditions at which a smaller group of phases can be arranged into a equilibrium with $\Delta G_{reaction}$ = 0. This requires a non-linear solver and starting guesses of phase compositions.

Pressure

Sillimanite

Andalusite

Perple_X: At this *PT* condition, $G_{sill} < G_{ky}$ or G_{and}

Perple_X: At this *PT* condition, $G_{sill} < G_{ky}$ or G_{and}

Perple_X: At this *PT* condition, $G_{sill} < G_{ky}$ or G_{and}

Perple_X: At this *PT* condition, $G_{sill} < G_{ky}$ or G_{and}

Perple_X: At this *PT* condition, $G_{and} < G_{ky}$ or G_{sill}

Temperature

Key strategy 1:

Gridded minimization

Perple_X presents the user with options to control how this works:

• *x_nodes* & *y_nodes* define the number of red dots

• *grid_levels* defines the amount of refinement of this grid
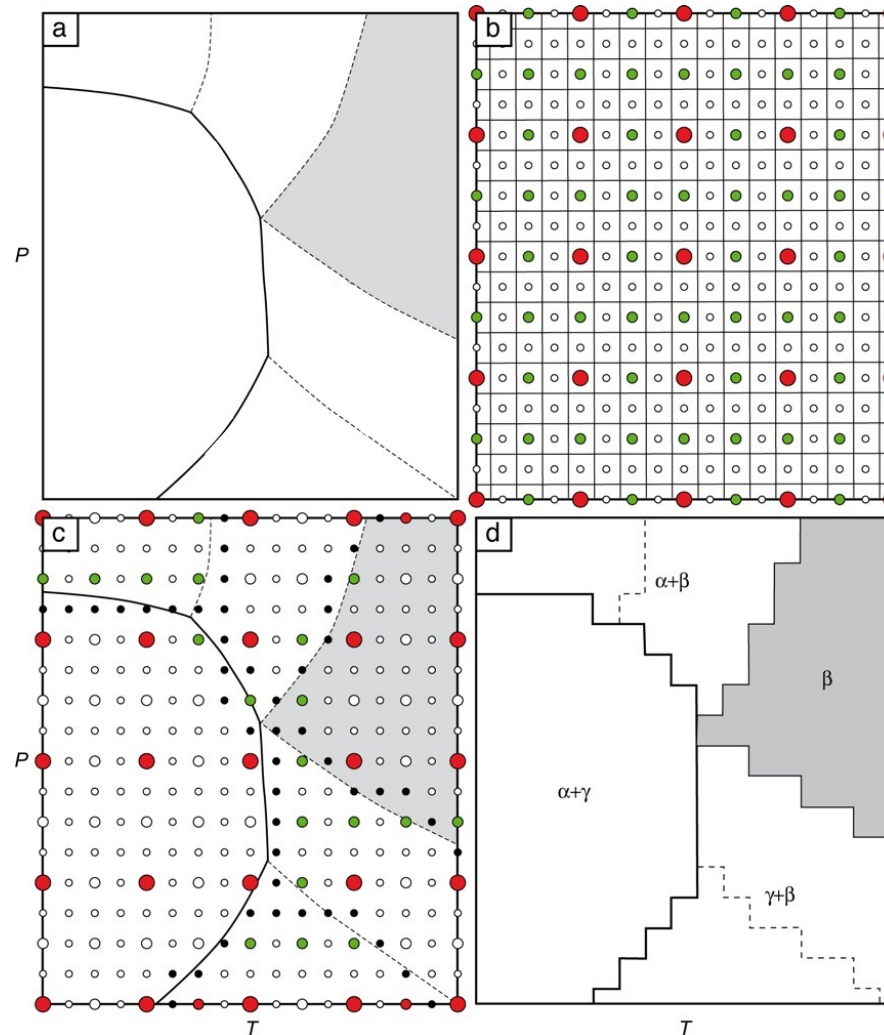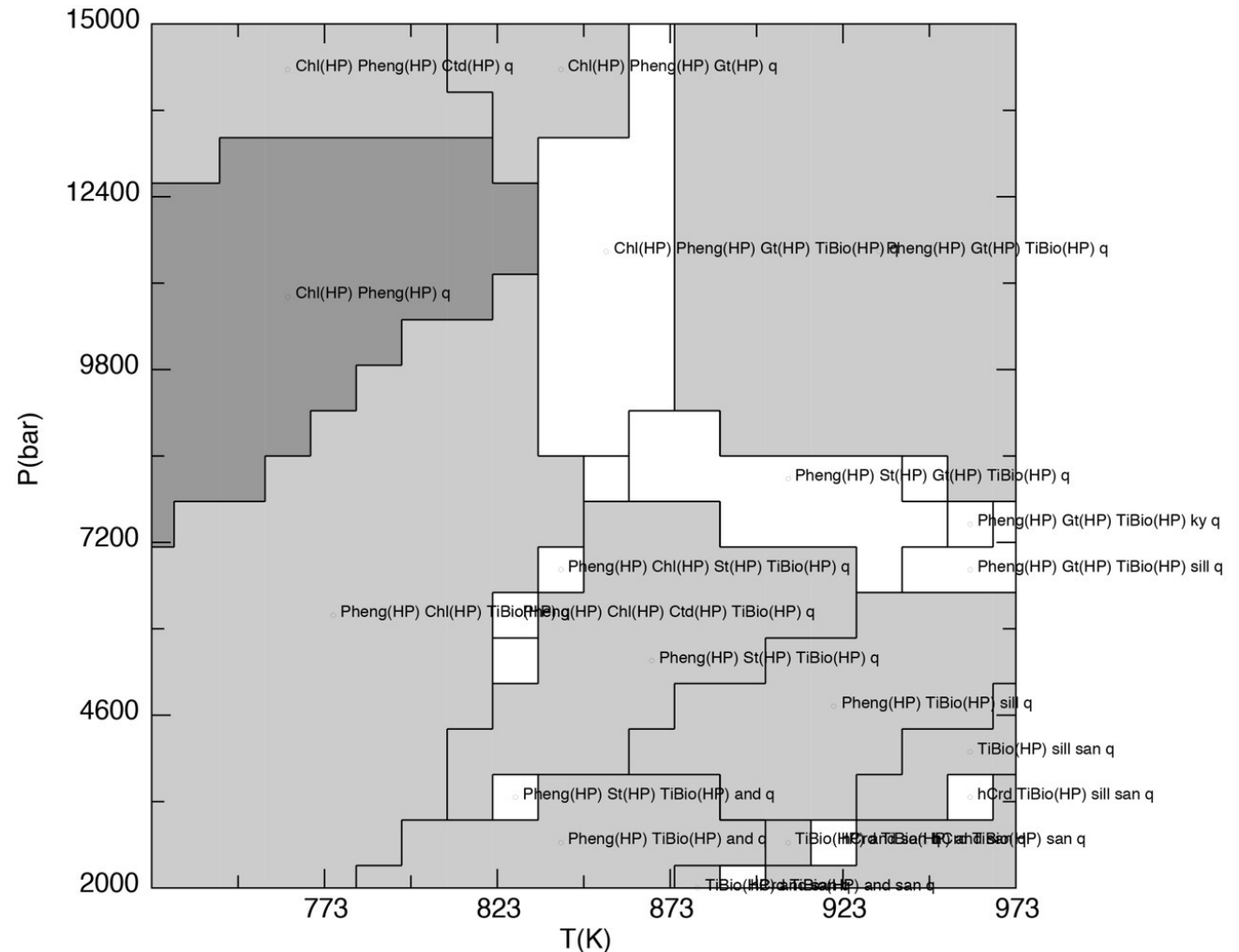
Key strategy 1:

Gridded minimization

Diagram calculated in KFMASH (K_2O-FeO-MgO-Al_2O3-SiO_2-H_2O). All fields also contain fluid.

Calculated with a 2002 update to the Holland & Powell (1998) dataset and mineral solution (a-X) models from THERMOCALC.

Calculation took ~5 minutes for me to setup and ~ 15 seconds for Perple_X to run.

Unmodified diagram shown.

Key strategy 1:

Gridded minimization

Diagram calculated in KFMASH (K_2O-FeO-MgO-Al_2O3-SiO_2-H_2O). All fields also contain fluid.

Calculated with a 2002 update to the Holland & Powell (1998) dataset and mineral solution (a-X) models from THERMOCALC.

Calculation took ~5 minutes for me to setup and ~ 90 seconds for Perple_X to run.

Unmodified diagram shown.
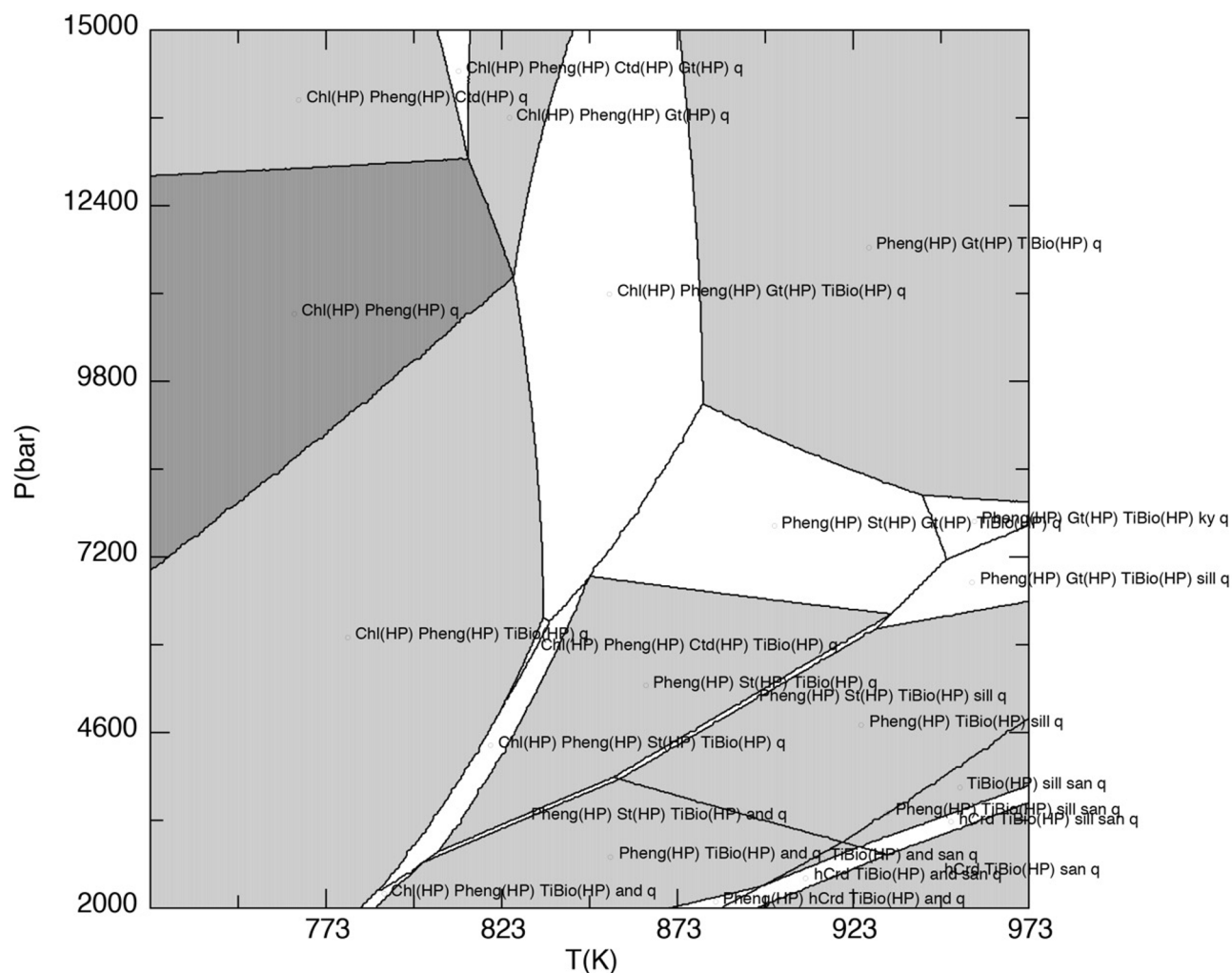
Key strategy 1:

Gridded minimization

Calculated considering CaO, MgO, FeO, SiO_2, H_2O and CO_2. Fluid saturated, with fluid composition on x-axis

Calculated with a 2002 update to the Holland & Powell (1998) dataset and mineral solution (a-X) models from THERMOCALC.

Calculation took ~5 minutes for me to setup and ~ 120 seconds for Perple_X to run.

Unmodified diagram shown.
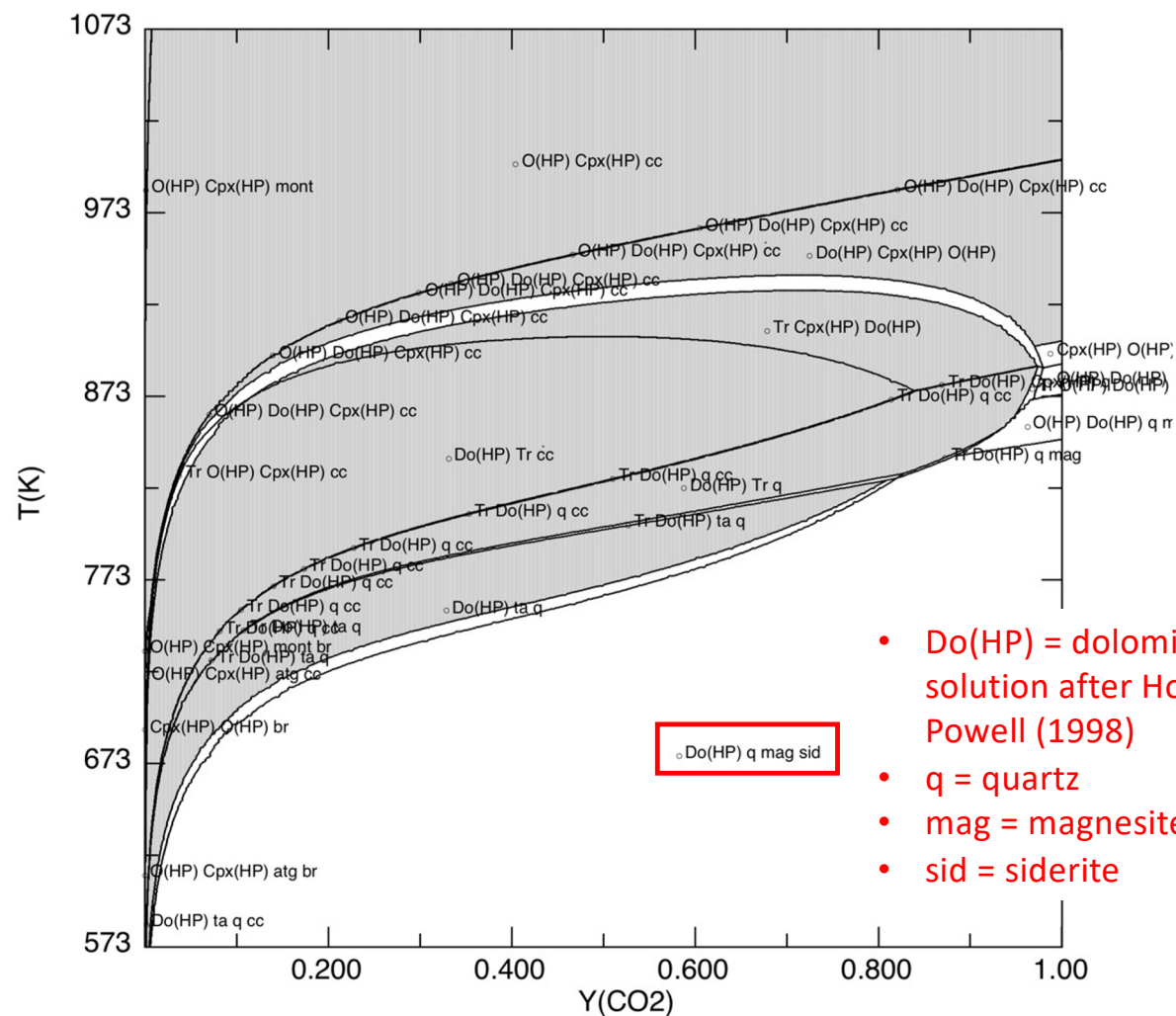
- Do(HP) = dolomite-ankerite solution after Holland & Powell (1998)
- q = quartz
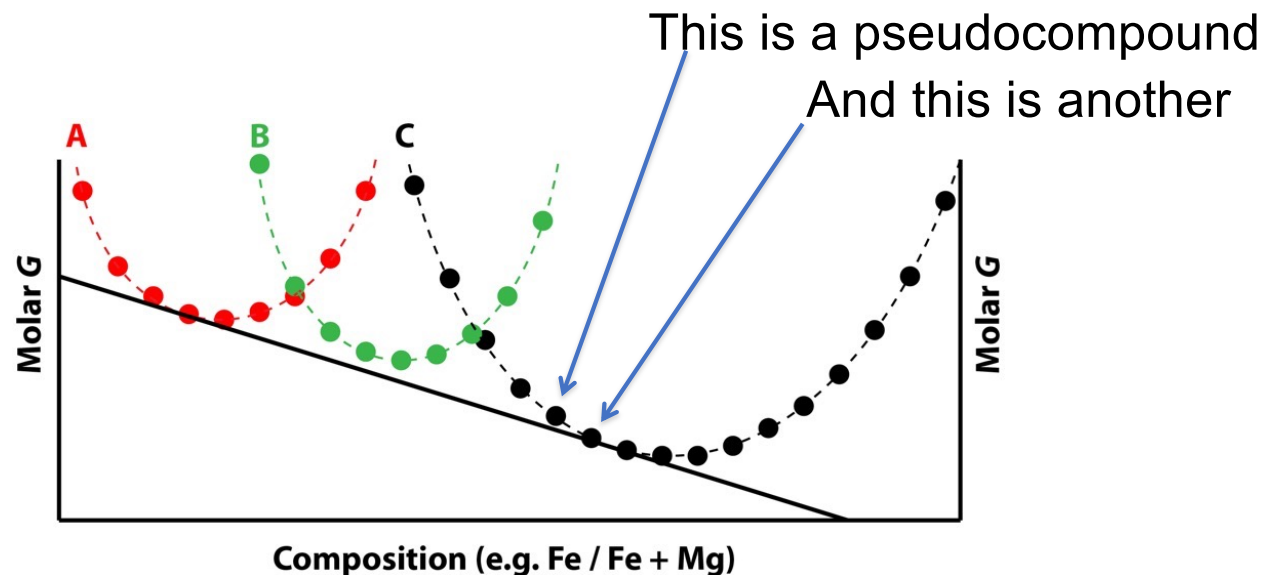- mag = magnesite
- sid = siderite

Perple_X's can solve problems like these because of a fundamental assumption… 'pseudocompounds'

This assumption is one of the reasons that Perple_X is so flexible and is also the source of many of its difficulties

Key strategy 2:

Pseudocompounds

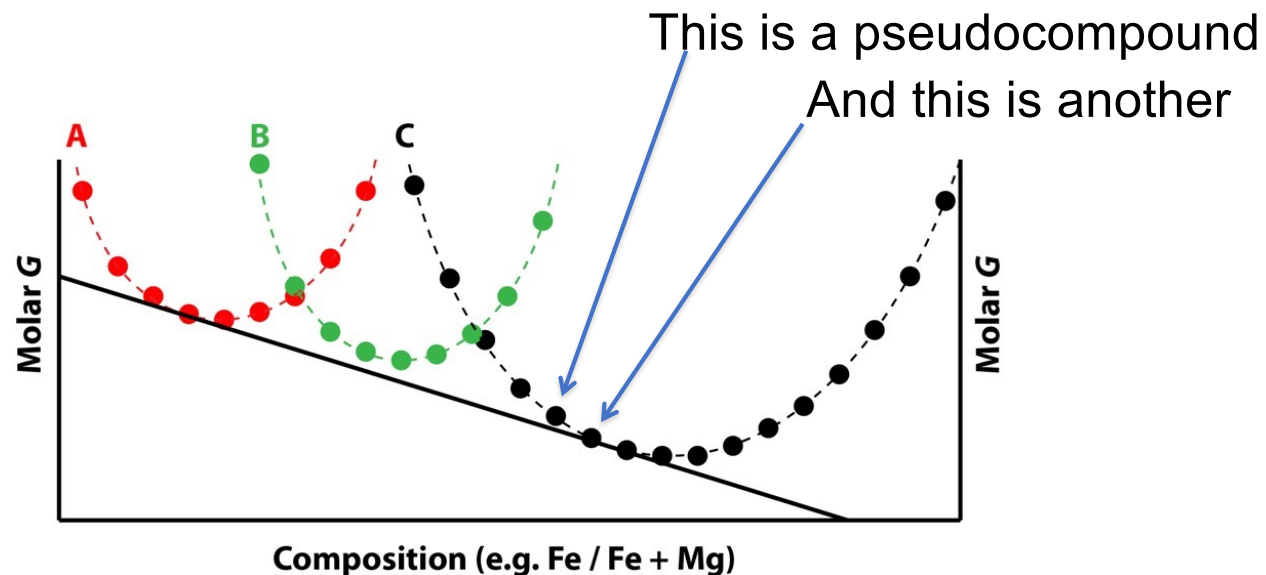This is a pseudocompound
And this is another

Perple_X generates these pseudocompounds across the solution space of every phase before minimization begins.

These define phase compositions for which G_{phase} can be easily calculated as a function of P and T.
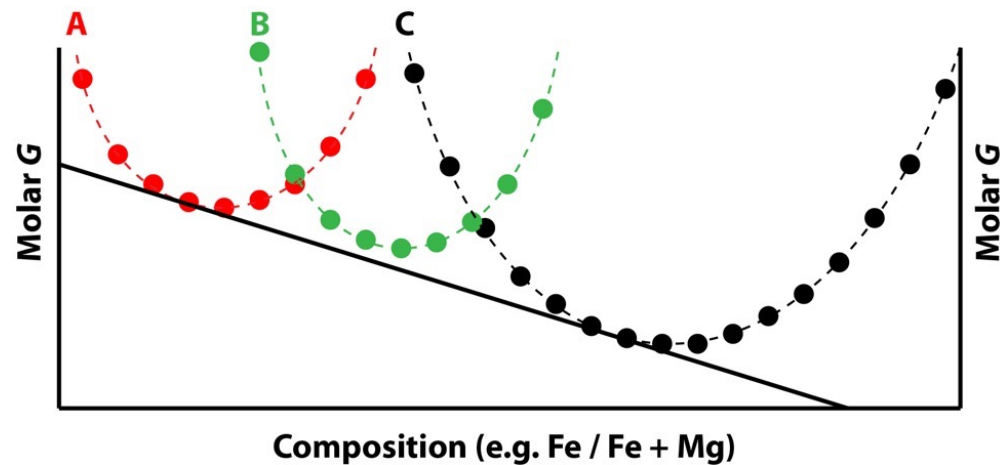
Key strategy 2:

Pseudocompounds

This is a pseudocompound
And this is another

Composition (e.g. Fe / Fe + Mg)

The minimizer then finds which set of pseudocompounds result in the lowest G_{system}, subject to the constraint that their compositions must sum to the system composition.
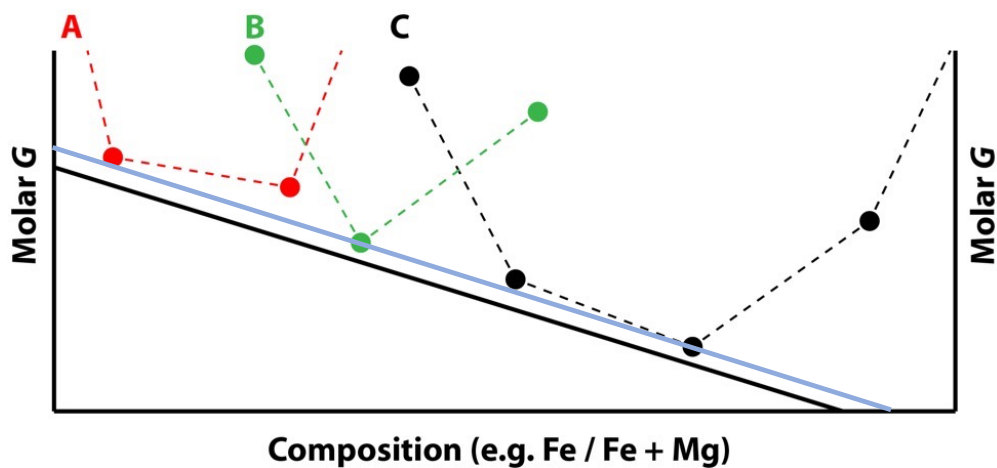
Key strategy 2:

Pseudocompounds

This approximation works well if the *G-X* surface for each phase is densely populated with pseudocompounds.
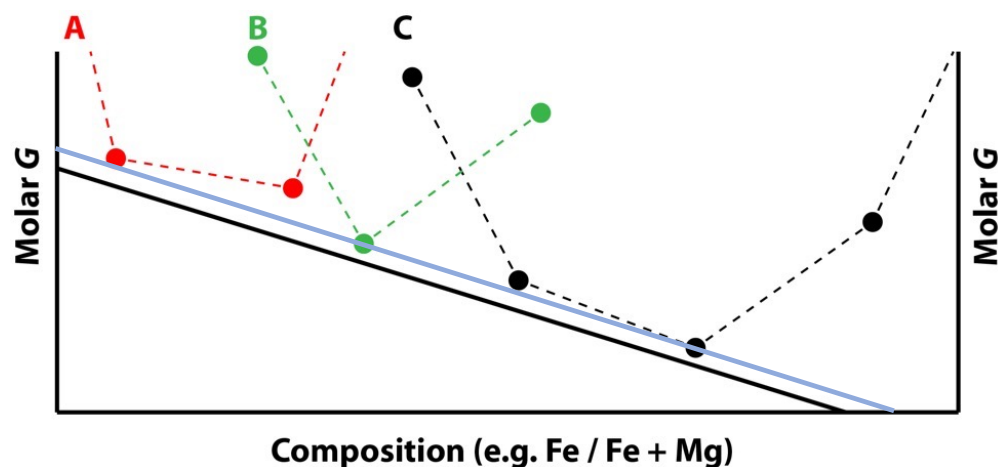
Key strategy 2:

Pseudocompounds

And poorly otherwise.
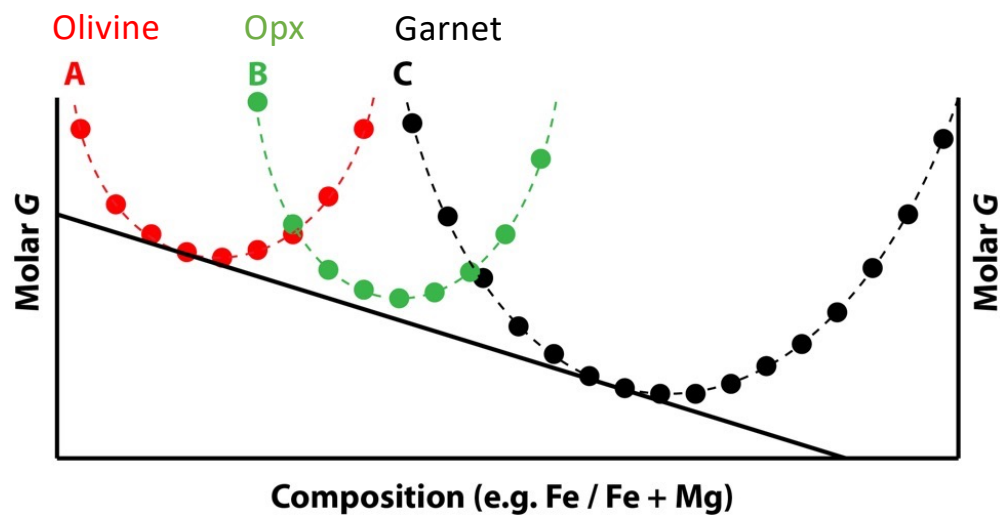
Key strategy 2:

Pseudocompounds

This matters, because each pseudocompound needs a little memory and adds a little time to the minimization.
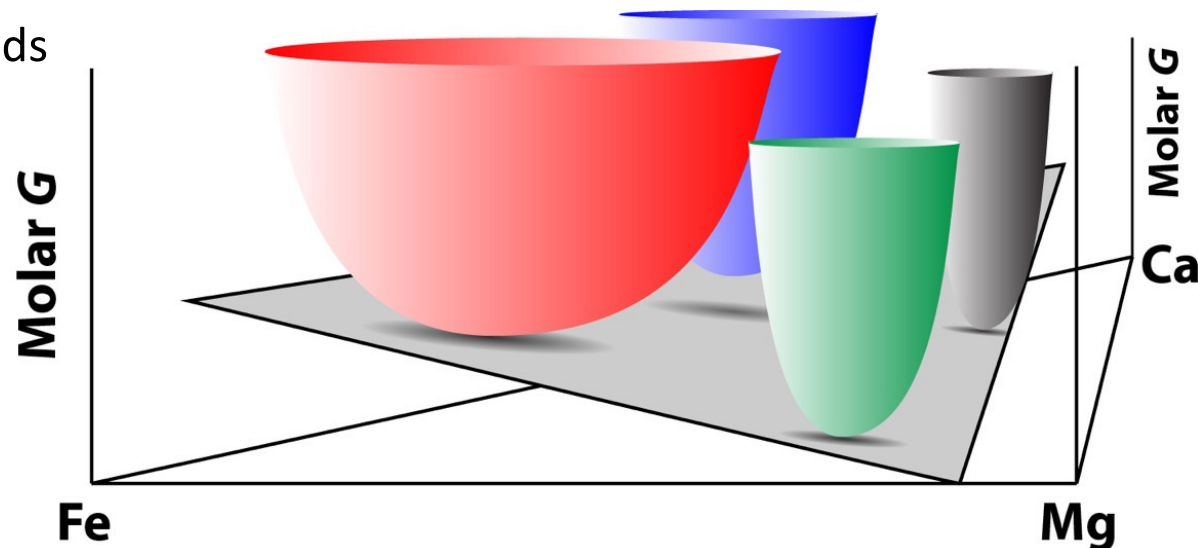
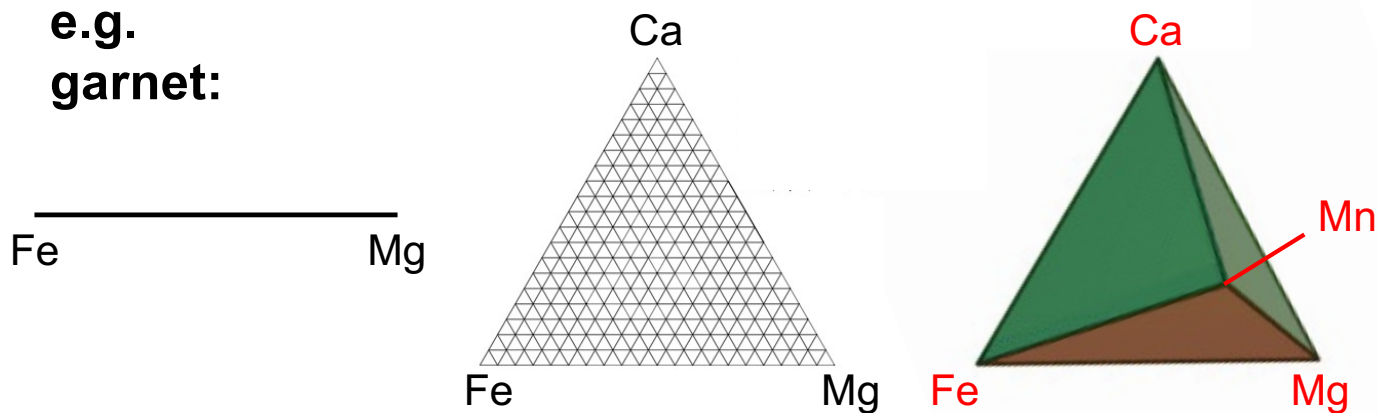# Key strategy 2:

Pseudocompounds

e.g.
garnet:

Fe ————————— Mg

Key strategy 2:

Pseudocompounds

e.g.
garnet:

Key strategy 2:

Pseudocompounds

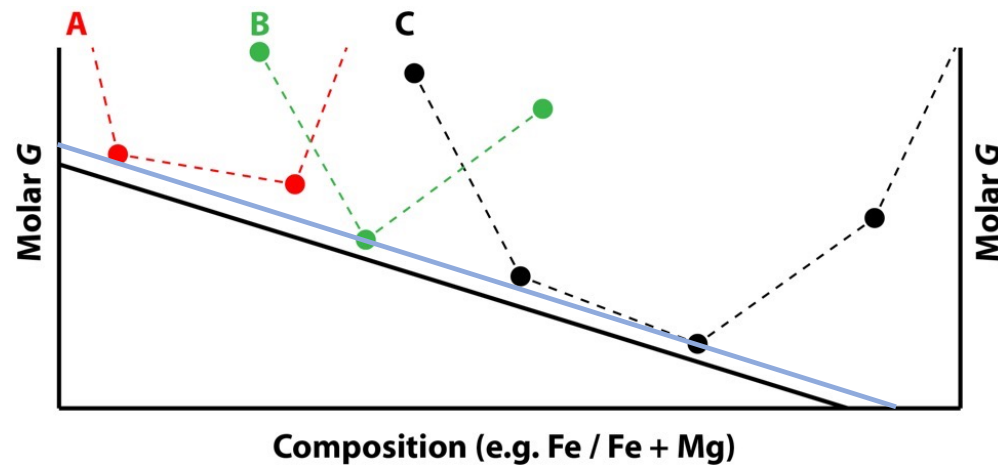Composition (e.g. Fe / Fe + Mg)

The White *et al* 2001 haplogranite melt model has 8 dimensions

8 dimensions = an enormous amount (potentially many millions) of pseudocompounds

An enormous amount of pseudocompounds = a huge memory and time requirement

Solid solution models in Perple_X

- **More pseudocompounds** (higher sampling density across each solution phase) is desirable for smoother tracking of *G-X* surfaces (up to a point) and thus smaller uncertainties and better phase boundaries

- **Fewer pseudocompounds** are desirable for more rapid calculation

- Sampling of complex (multi-dimensional, e.g. amphibole or melt) phases can easily produce $> 10^6$ pseudocompounds – which requires more memory than most computers have (or will allow)

- Perple_X and its helper program Paralyzer have strategies for handling this

Solid solution models in Perple_X

Two main approaches solve this requirement of balancing 'less' with 'more' (calculations could take days if we're not careful):
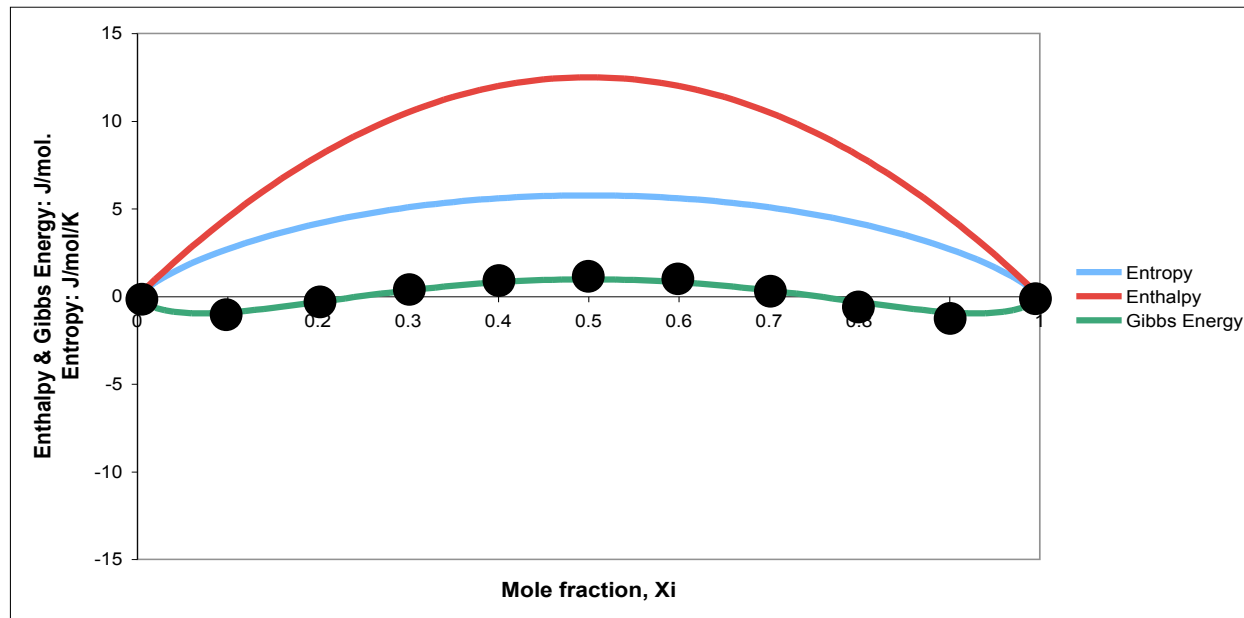
- 'Adaptive refinement'
- 'Pseudocompound iteration'
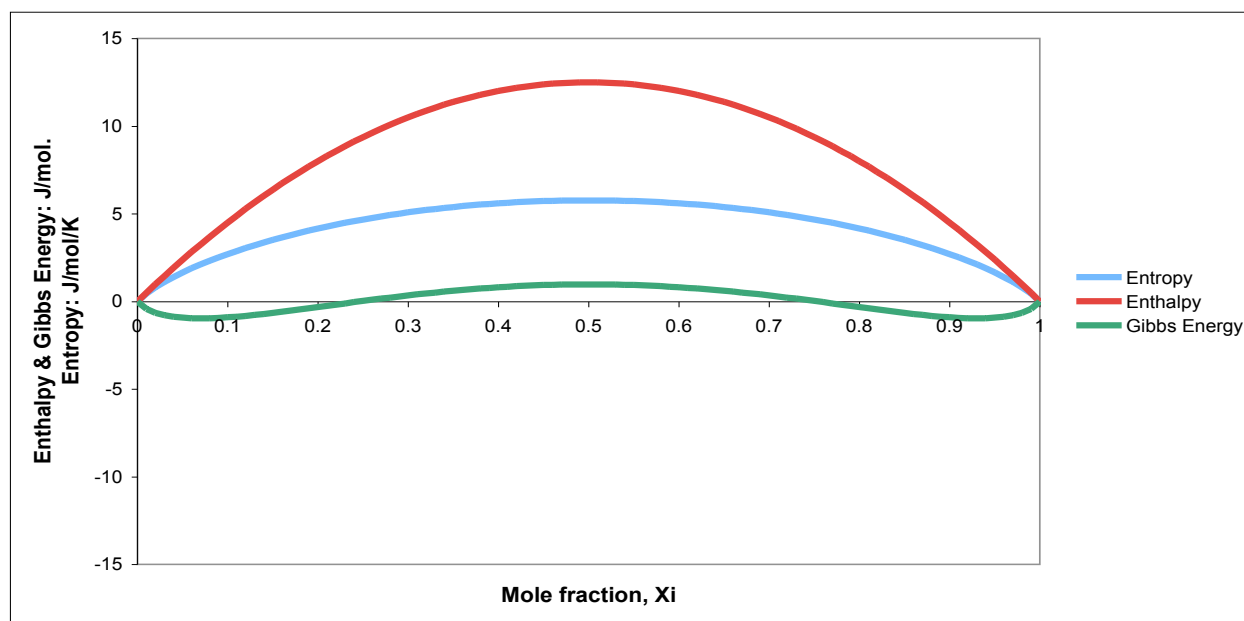
Solid solution models in Perple_X

Strategy I: **'adaptive refinement'**

1. *do a few minimizations at low compositional resolution to create a 'rough' P-T diagram*

Solid solution models in Perple_X

Strategy I: 'adaptive refinement'

2. *use this to guide the code where the ranges of stable phase compositions are for the P-T-X of interest, discarding other possible phase compositions*

Apparent stable range of phase
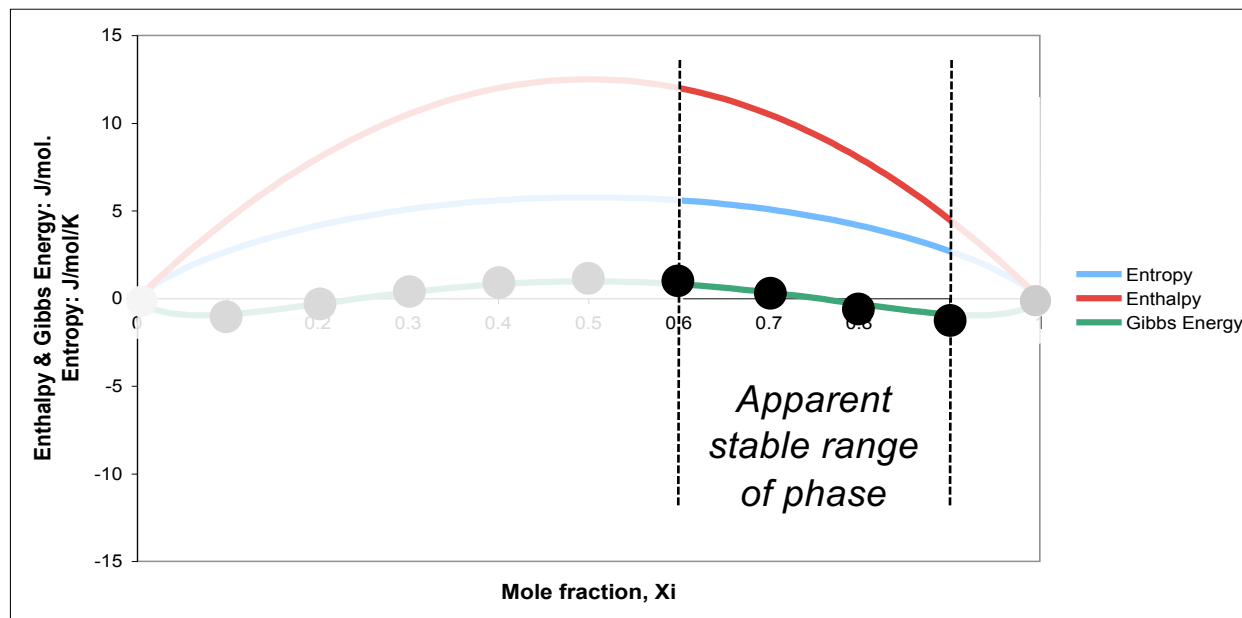
Solid solution models in Perple_X

Strategy I: **'adaptive refinement'**

3. *re-do the calculation, but only for the range of 'apparently stable compositions', and at significantly higher resolution*
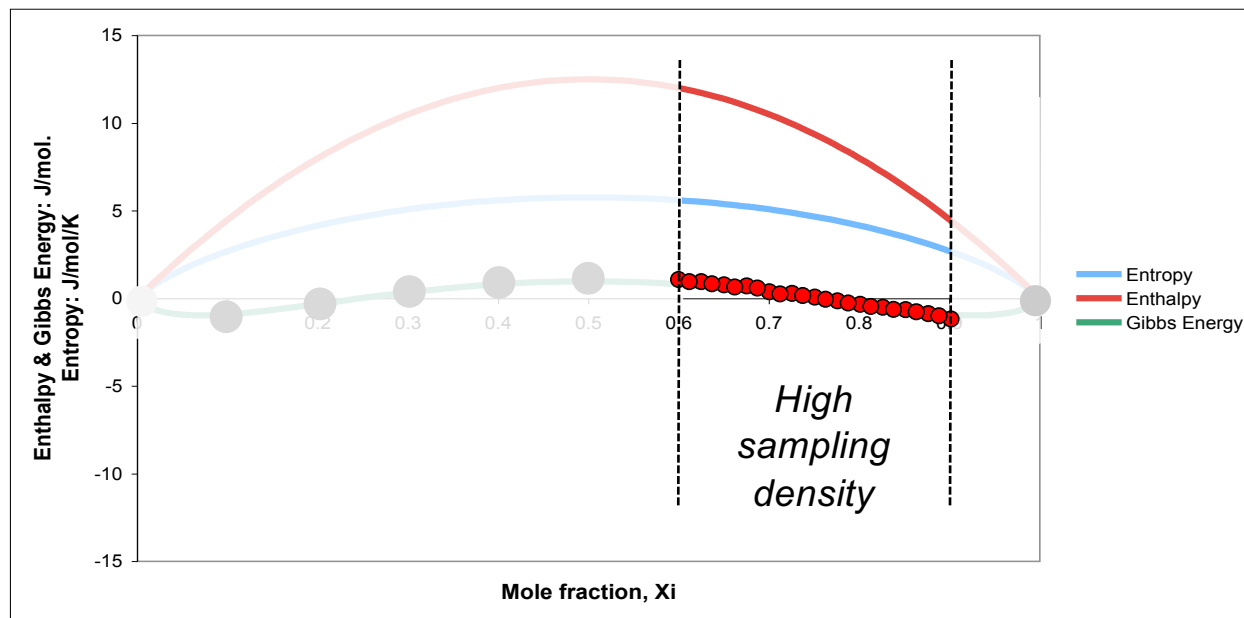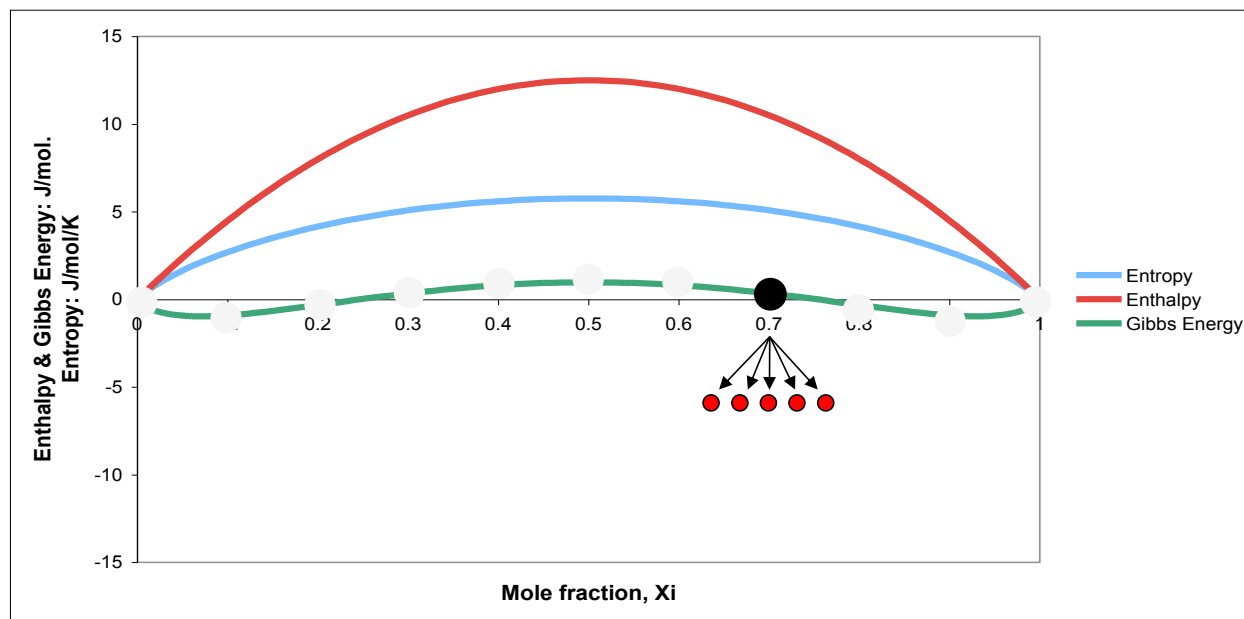
Solid solution models in Perple_X

Strategy II: 'pseudocompound iteration'

If a pseudocompound of a phase seems to be stable in a minimization at any one P & T, make extra pseudocompounds around it and try again
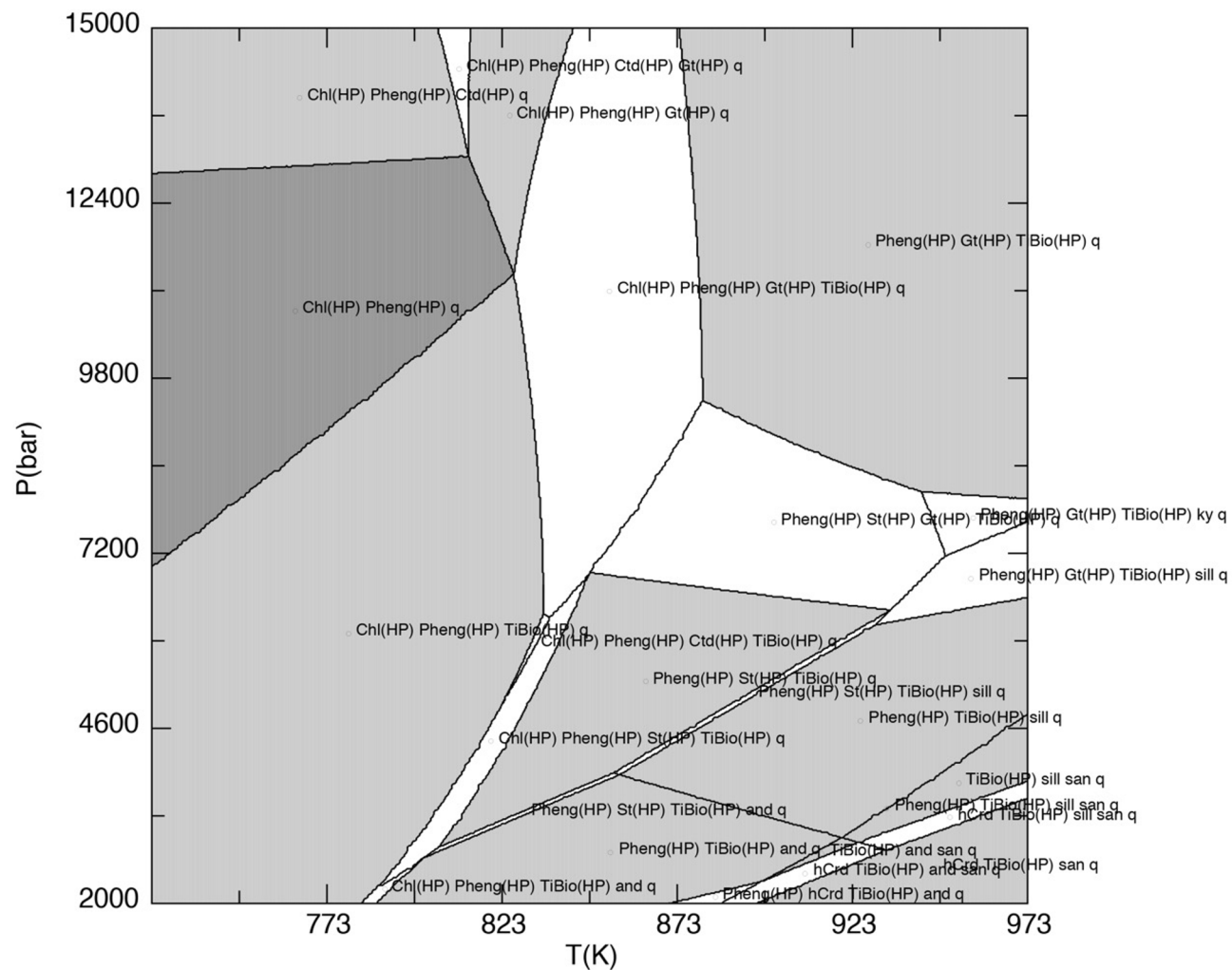
Benefits:

Automatically finds the lowest free energy surface

Little chance of mistakenly calculating a meta-stable phase diagram…
(but what if you want to do that)?

Requires almost no user input once the calculation parameters have
been defined

Weaknesses:

Less useful as a pedagogical tool than THERMOCALC

Every end-member in your dataset of choice is considered (revealing
areas of PT space in which their calibration 'fails')

Minimization can take many hours

In practice, what does a calculation look like?

Build

(Problem setup)

Vertex

(Free energy minimisation)

Meemum

(single *PT* point stability calculator)

Pssect

(Postscript plot generator)

Werami

(Secondary data extraction)

Illustrator/Coreldraw/etc

(Making it look better)

Matlab (pscontor)

Contouring routine
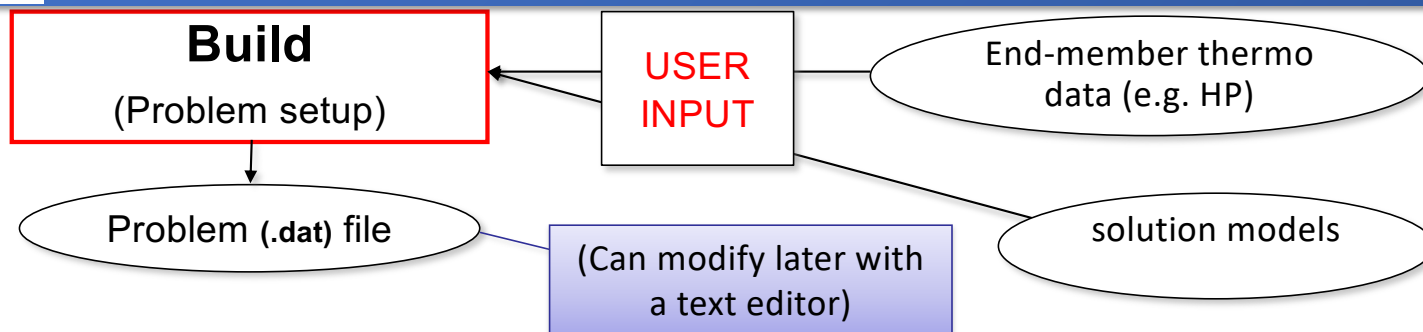
'USER INPUT' includes:

- What chemical system should Perple_X use?

- Are fluids or phases saturated?

- What equation of state for fluid? Should we do anything else special with fluid?

- What are the axes of the diagram (P, T, X, f, a, μ, etc)?

- What thermodynamic dataset and what equations for solution phases (a-X models)?

PHASE EQUILIBRIUM MODELLING:
APPROACHES AND PITFALLS

What end-member and *a-X* models are available?

- Berman 1988 (and subsequent revisions)
- Berman and Aranovich 1996 (the TWQ database)
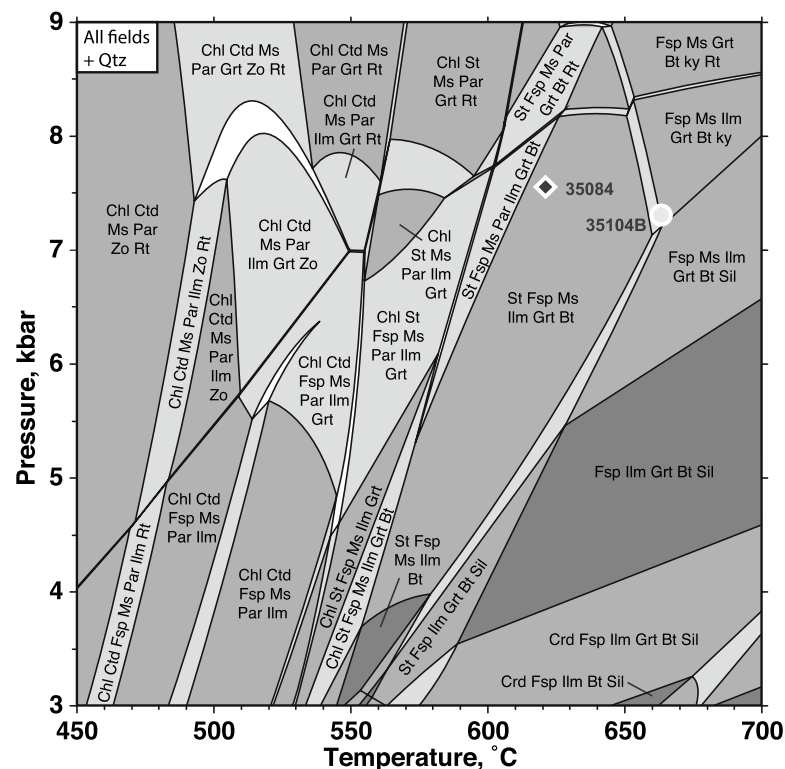
- Multiple versions of the THERMOCALC (Holland & Powell) database from 1998 onwards

- Versions of both Berman and H&P supplemented with the Harrison & Sverjensky (2013) Deep Earth Water database

- Versions of H&P data supplemented with shear moduli from Kerrick & Connolly (2002)

Farber et al., 2014

What end-member and *a-X* models are available?

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- Multiple versions of the THERMOCALC (Holland & Powell) database from 1998 onwards

- Versions of both Berman and H&P supplemented with the Harrison & Sverjensky (2013) Deep Earth Water database

- Versions of H&P data supplemented with shear moduli from Kerrick & Connolly (2002)

- Supcrt92

(a) 200 ℃

1: Ol Atg Mag Bn
2: Brc Atg Mag Bn
3: Brc Atg Bn Hem
4: Brc Atg Mag Ccp
5: Brc Atg Ccp Po
6: Brc Py Atg Ccp
7: Brc Py Atg Bn
8: Ol Atg Ccp Po
9: Ol Py Atg Ccp
10: Ol Py Atg Bn
11: Ol Py Tcl Ccp
12: Ol Py Tcl Bn
13: Ol Cv Py Tcl

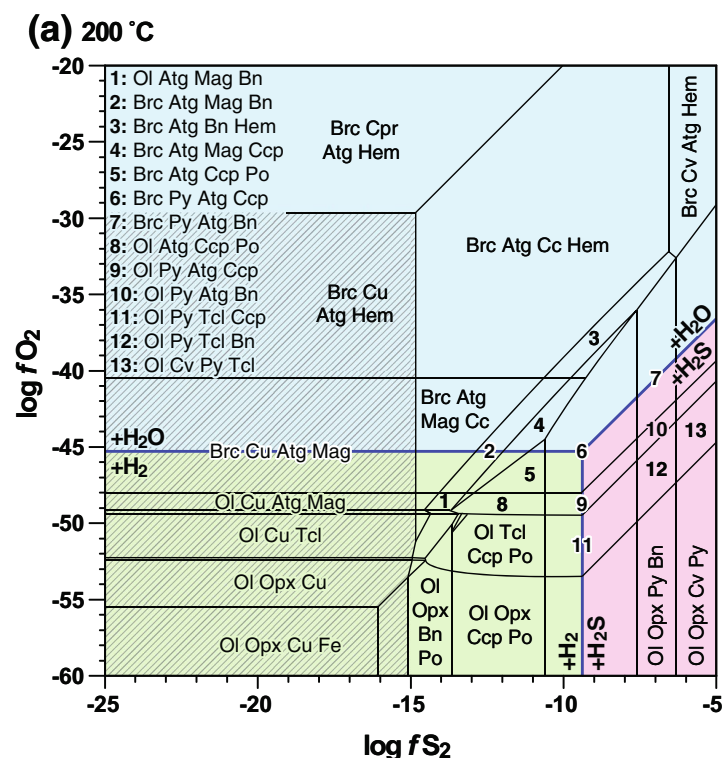# What end-member and *a-X* models are available?

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- Berman and Aranovich 1996 (the TWQ database)

- Multiple versions of the THERMOCALC (Holland & Powell) database from 1998 onwards

- Versions of both Berman and H&P supplemented with the Harrison & Sverjensky (2013) Deep Earth Water database

- Versions of H&P data supplemented with shear moduli from Kerrick & Connolly (2002)

- Supcrt92

- Stixrude & Lithgow-Bertelloni (2011)

Adam et al., 2017
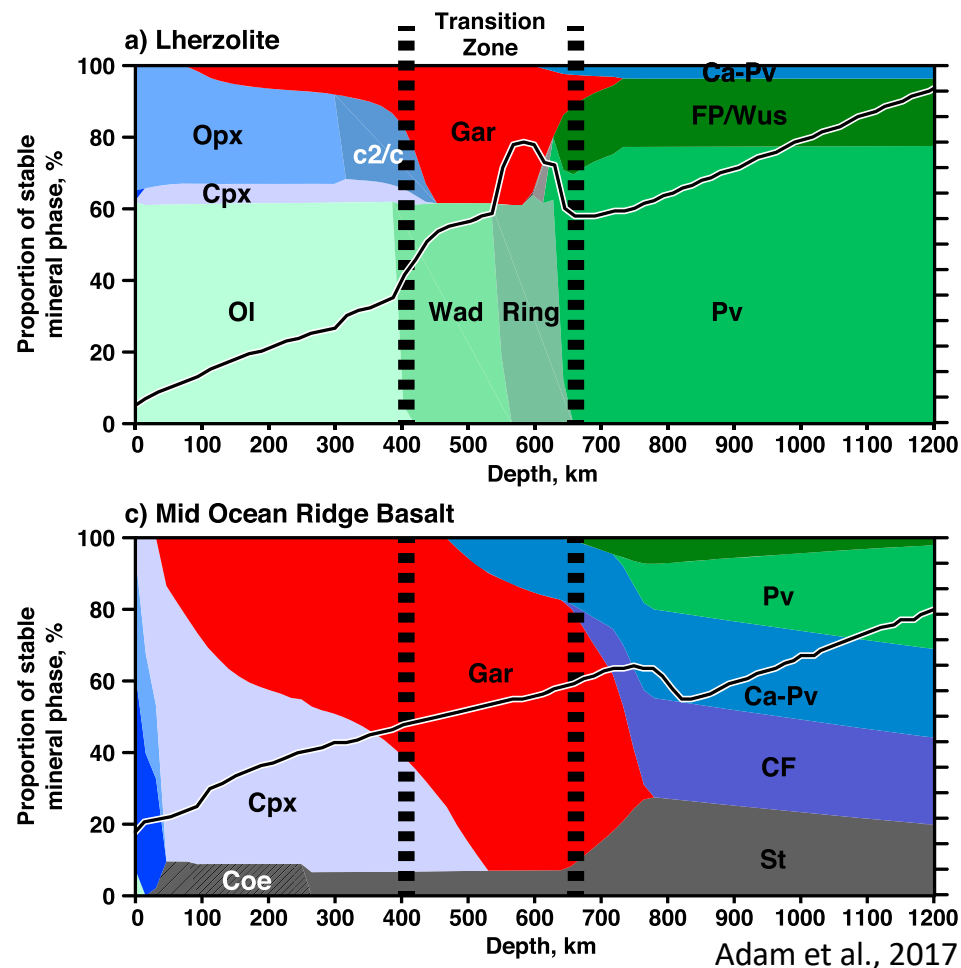
An extract of a thermodynamic data table formatted for Perple_X

EOS 2 = normal polynomials for α, C_P, K_T; Murnaghan for V (e.g., Holland & Powell 1998)

Reference state G, S and V

$C_P(T,P_r) = c1 + c2 \cdot T + c3/T^2 + c4 \cdot T^2 + c5/T^{1/2}$

```
fa      EoS = 2
SIO2(1)FEO(2)
G0 = -1378935 S0 = 151 V0 = 4.631
c1 = 201.1 c2 = .1733E-1 c3 = -1960600 c5 = -900.9
b1 = .505E-4 b5 = -.505E-3 b6 = 1330000. b7 = -199.5 b8 = 4
end


teph    EoS = 2
SIO2(1)MNO(2)
G0 = -1631705 S0 = 155.9 V0 = 4.899
c1 = 219.6 c3 = -1292700 c5 = -1308.3
b1 = .505E-4 b5 = -.505E-3 b6 = 1200000. b7 = -180 b8 = 4
end
```

The isobaric expansivity (α) at the reference pressure is

$$\alpha(T,P_r) = b1 + b2 \cdot T + b3/T + b4/T^2 + b5/T^{1/2}$$

Volume at the reference pressure is

$$V(T,P_r) = V0 \cdot [1 + integral(\alpha(T,P_r), T=T_r..T)]$$

A simple activity-composition model, formatted for Perple_X

```
begin_model
O(HP)                   | HP '98 olivine solution
2                       | model type: Margules, macroscopic

3                       | 3 endmembers
teph    fo     fa
 0 0 0                  | endmember flags

0.0 1.0  0.1   1                   | range and resolution for X(Mn), imod = 1 ->
                                        asymmetric transform subdivision
0.0 1.0  0.1   0                   | range and resolution for X(Mg), imod = 0 -> cartesian
                                        subdivision

begin_excess_function
W(fo fa) 8400. 0. 0.
end_excess_function

1                       1 site entropy model

3 2.                    3 species, site multiplicity = 2.
z(mg) = 1 fo
z(fe) = 1 fa

end_of_model
```

A simple activity-composition model, formatted for Perple_X

```
-----------------------------------------------------
begin_model

Gt(WPPH)                       | Ca-Fe2+-Mg-Al-Fe3+ Garnet model after White, Pomroy,
                                 Powell & Holland (JMG, 2005)


7                              | model type: Margules with dependent endmembers .

2                              | the number of independent subcompositions, reciprocal
                                 solution if > 1.


4  2                           | 4 species on site 1, 2 species on site 2.
                               | M2 and M1 can be identified as sites 1 and 2, respectively.
                               | the species that mix on site 1 are Mn-Mg-Fe-Ca and the
                               | species that mix on site 2 are Al-Fe3+.


spss  alm    py   gr           | endmember names
fmn_i  fkho_i  kho   andr_i

3                              | number of dependent endmembers

andr_i = 1 kho  - 1 py   +1 gr
fkho_i = 1 kho  + 1 alm  -1 py
fmn_i  = 1 kho  + 1 spss -1 py

0 0 0 0 0 0 0 0       | endmember flags
```

(…Continued)

```
0. .2  0.1 1              | imod = 0 -> cartesian subdivision (xmn) on X
0. 1.  0.1 0             | imod = 0 -> cartesian subdivision (xfe) on X
0. 1.  0.1 0             | imod = 0 -> cartesian subdivision (xmg) on X
0. 1.  0.1 0             | imod = 0 -> cartesian subdivision x(fe3+) on Y


-----------------------------------------------------
begin_excess_function
w(alm py)   2.5d3 0. 0.
w(alm kho)  22.5d3 0. 0.
w(py gr)    33d3 0. 0.
w(gr kho)   -7d3 0. 0.
w(spss kho) 20d3 0. 0.
end_excess_function

2                            |2 site entropy model

4 3.                         |4 species, site multiplicity 3
z(x,mn) = 1 spss
z(x,fe) = 1 alm
z(x,ca) = 1 gr

2 2.                         |2 species, site multiplicity 2
z(y,al) = 1 spss + 1 alm + 1 py + 1 gr

end_of_model
```
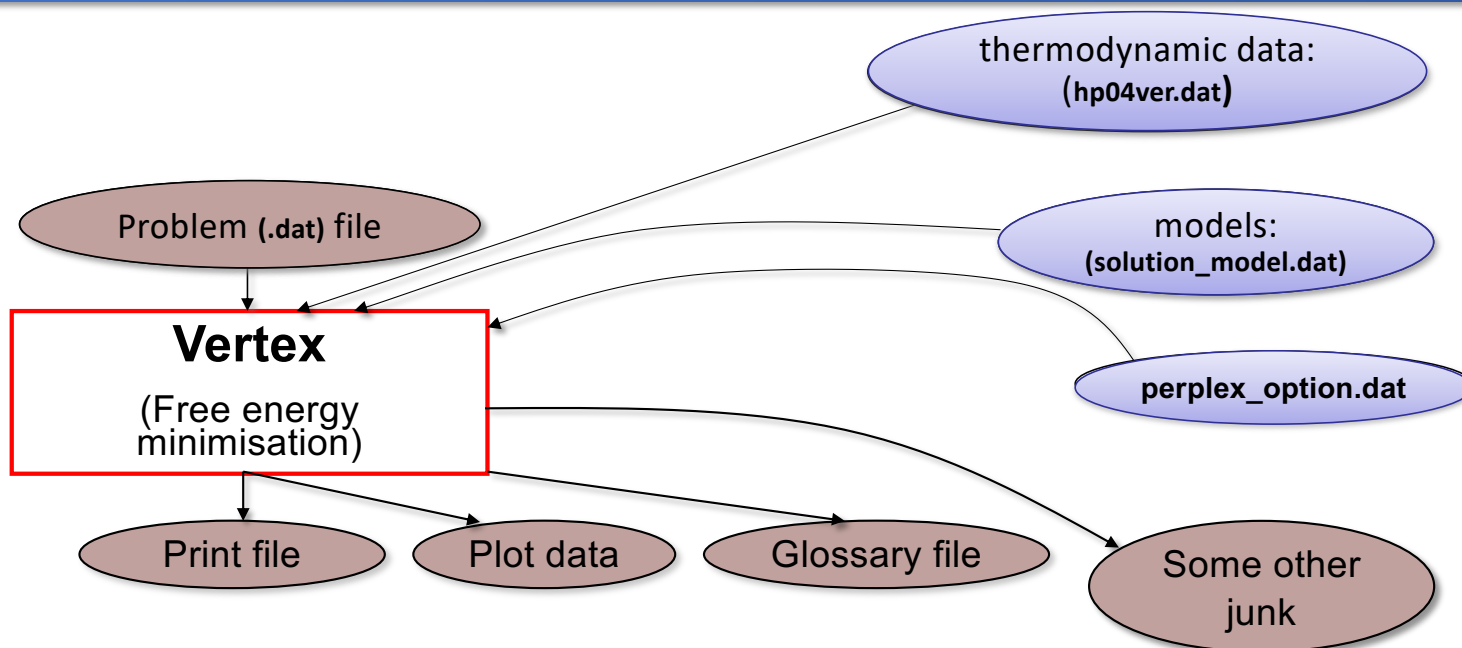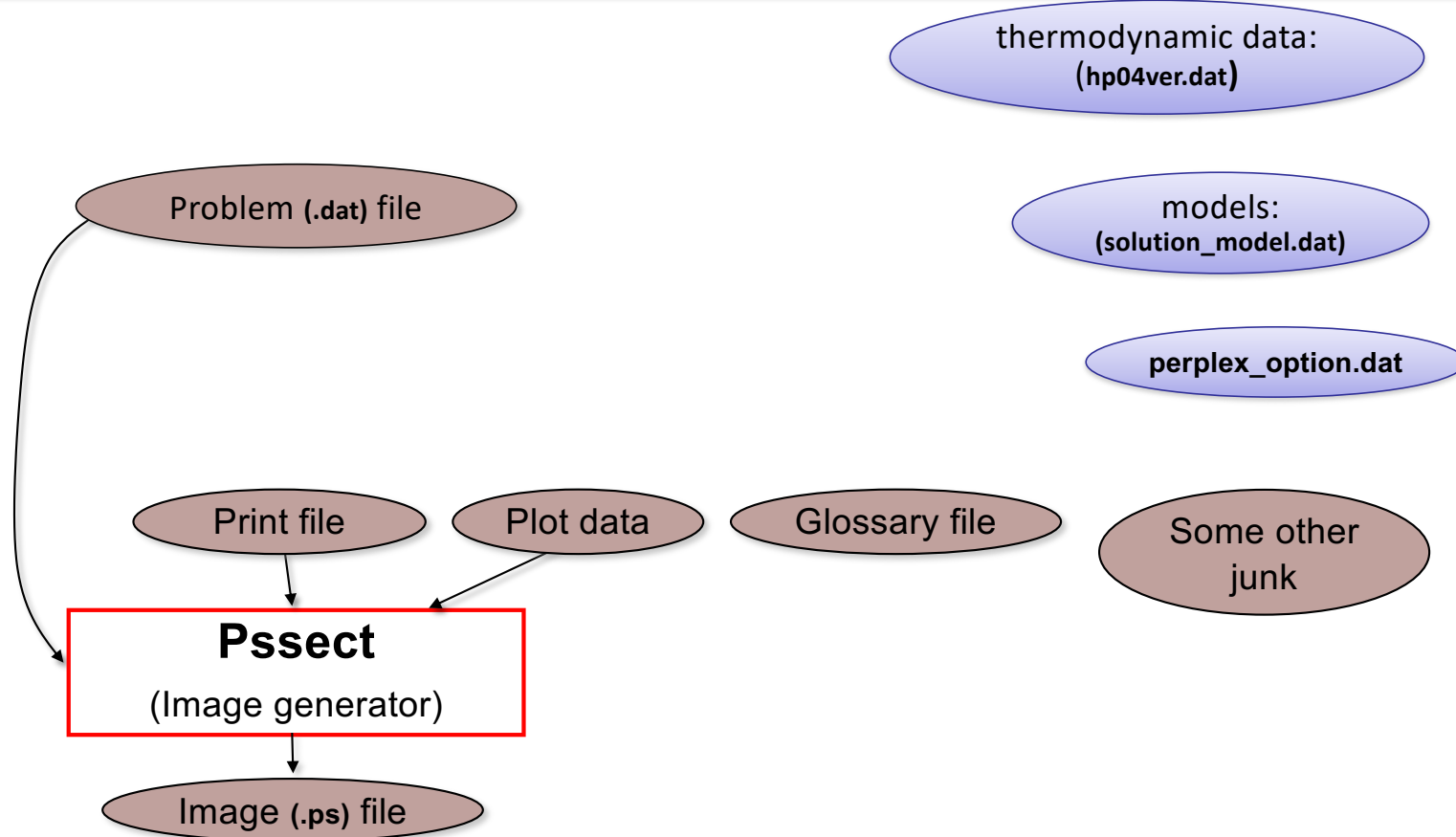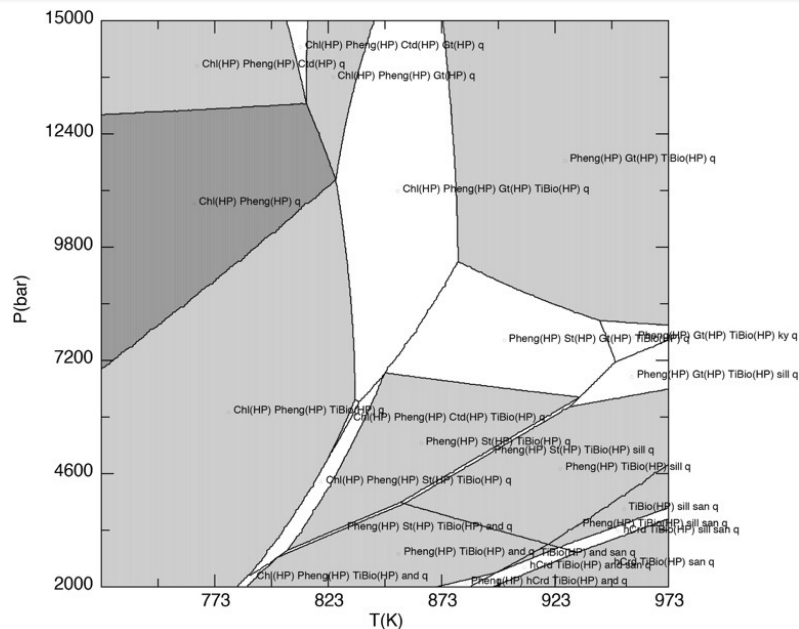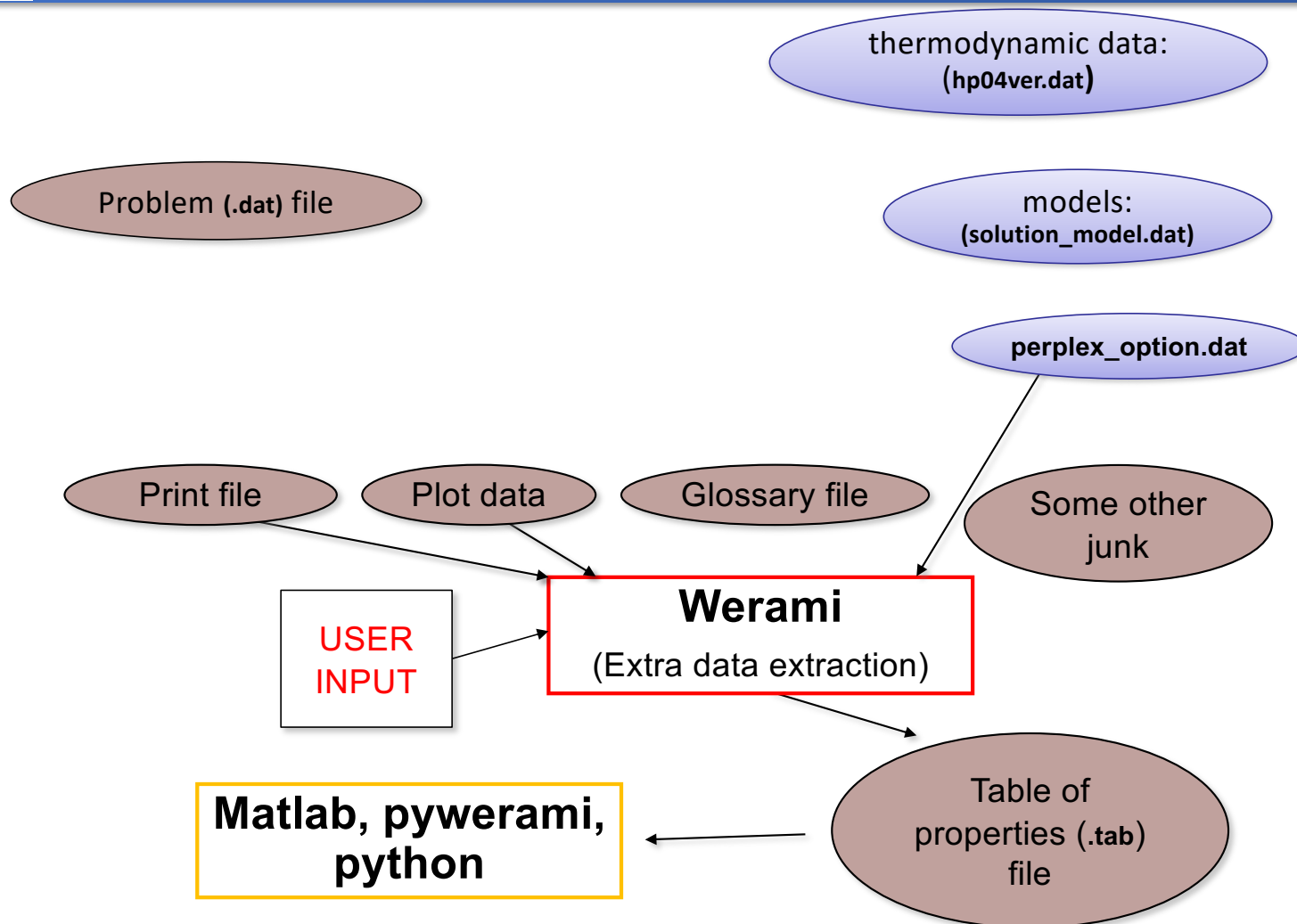
thermodynamic data:
(**hp04ver.dat**)

models:
(**solution_model.dat**)

perplex_option.dat

Problem **(.dat)** file

Print file

Plot data

Glossary file

Some other junk

Pssect
(Image generator)

Image **(.ps)** file

Pssect

(Image generator)

Image **(.ps)** file

thermodynamic data:
(**hp04ver.dat**)

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Glossary file

Some other junk

thermodynamic data:
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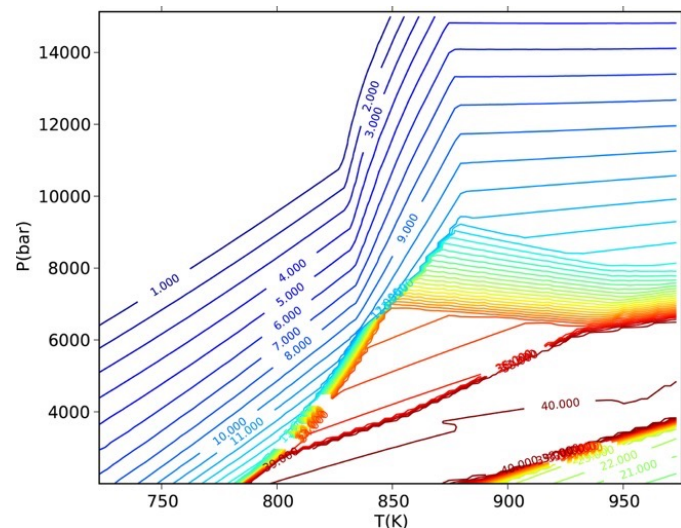(**solution_model.dat**)

perplex_option.dat

Print file   Plot data   Glossary file   Some other junk

USER INPUT

Werami
(Extra data extraction)

Matlab, pywerami, python

Table of properties **(.tab)** file
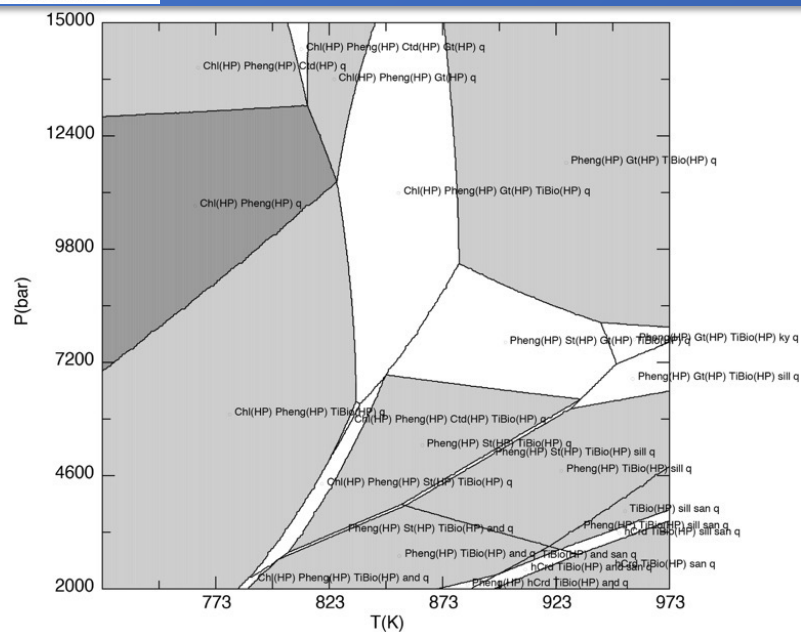
Modal proportion biotite

USER INPUT → **Werami** (Extra data extraction) → Table of properties (**.tab**) file → **Matlab, pywerami, python**

Can Perple_X replicate results calculated with THERMOCALC?

- Can the code do it?

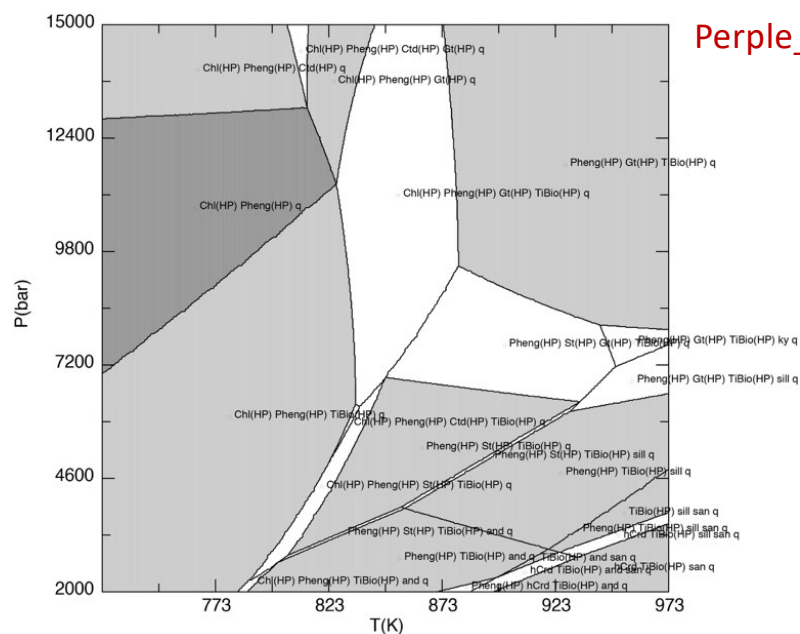- Can the user set up the problem with exactly the same parameters?
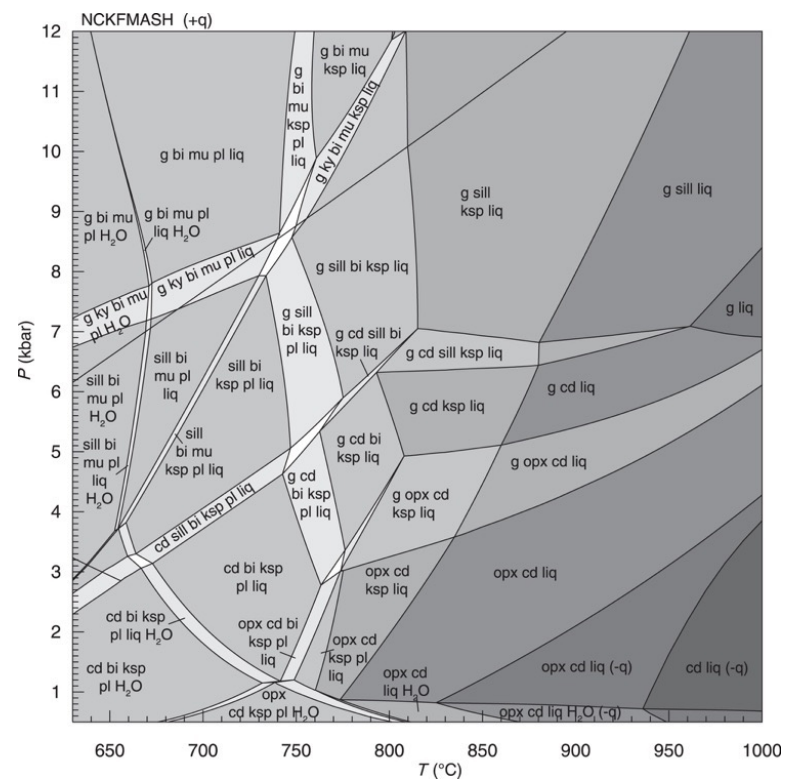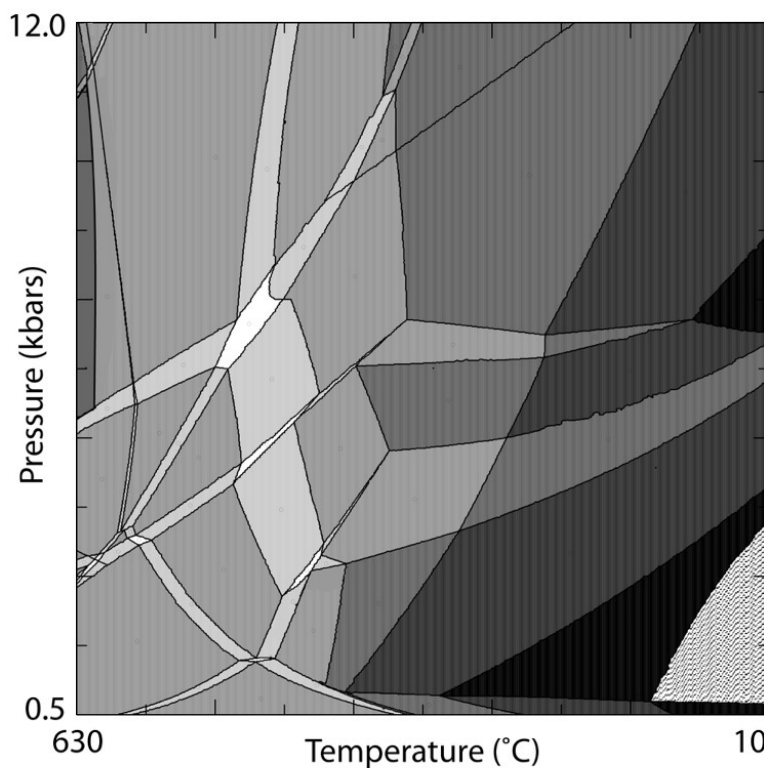

THERMOCALC
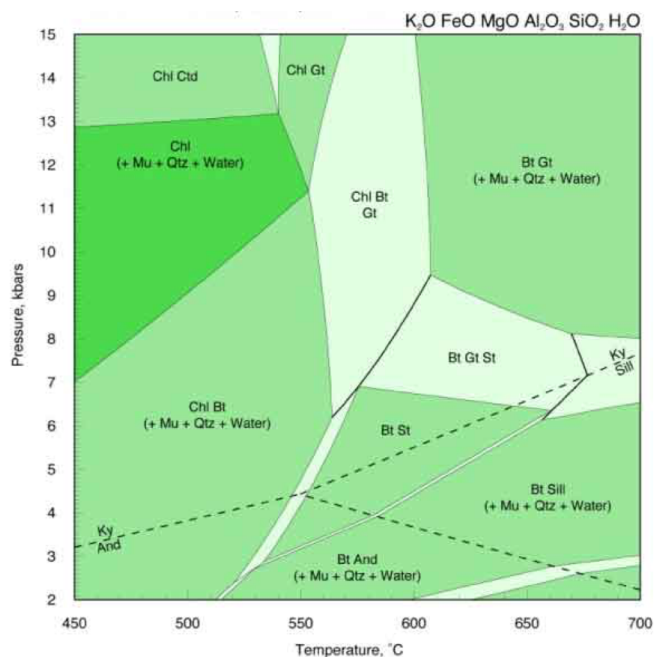
Perple_X

Figure 6 of White, Powell & Holland's 'Progress relating to calculation of partial melting equilibria for metapelites', *Journal of Metamorphic Geology* 2007.   Melt-bearing, Na-Ca-KFMASH
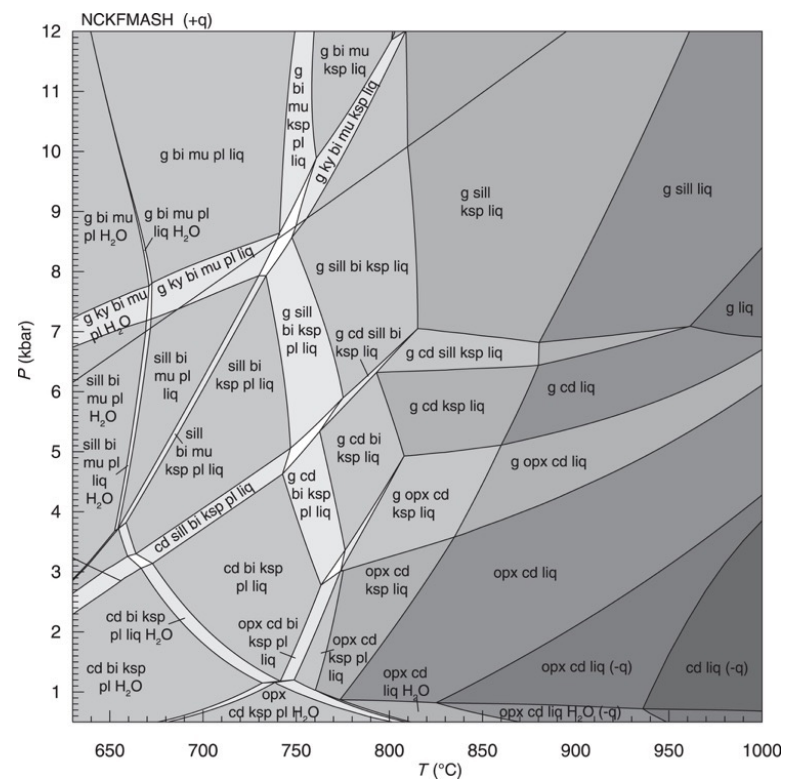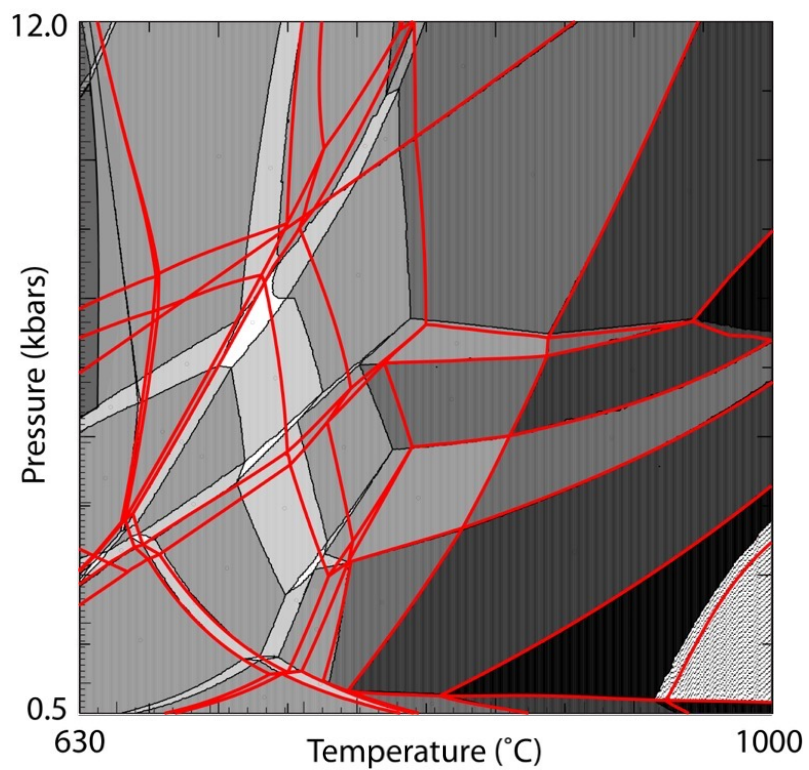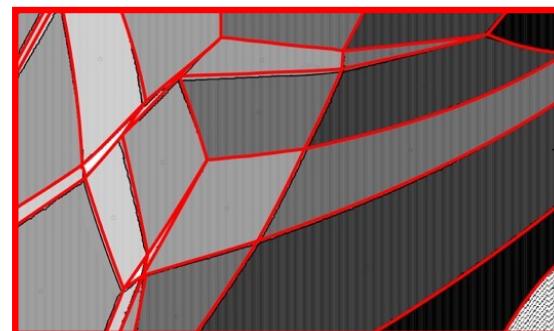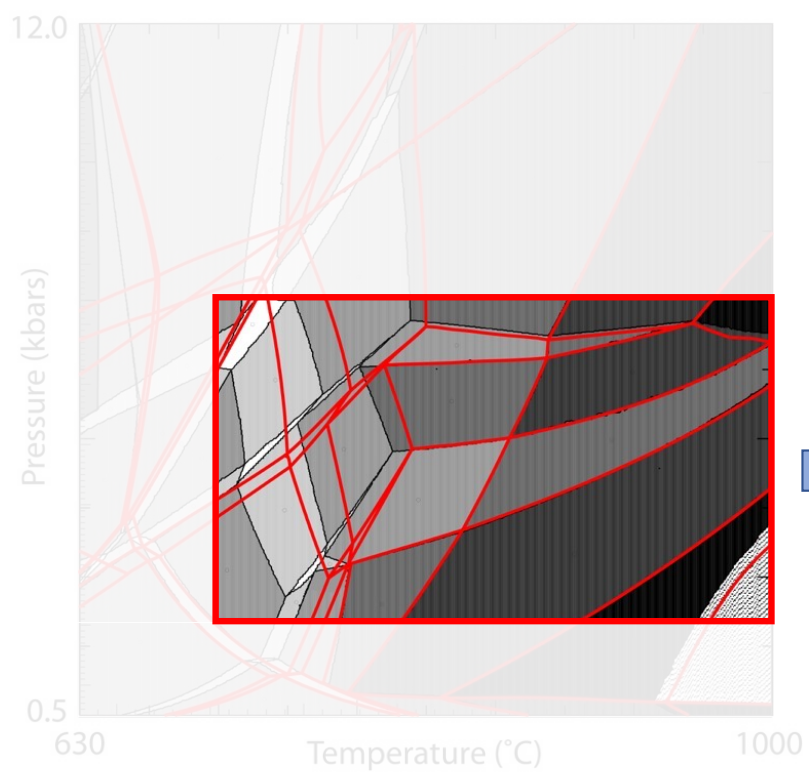

Perple_X version, approximately 5 hours calculation time

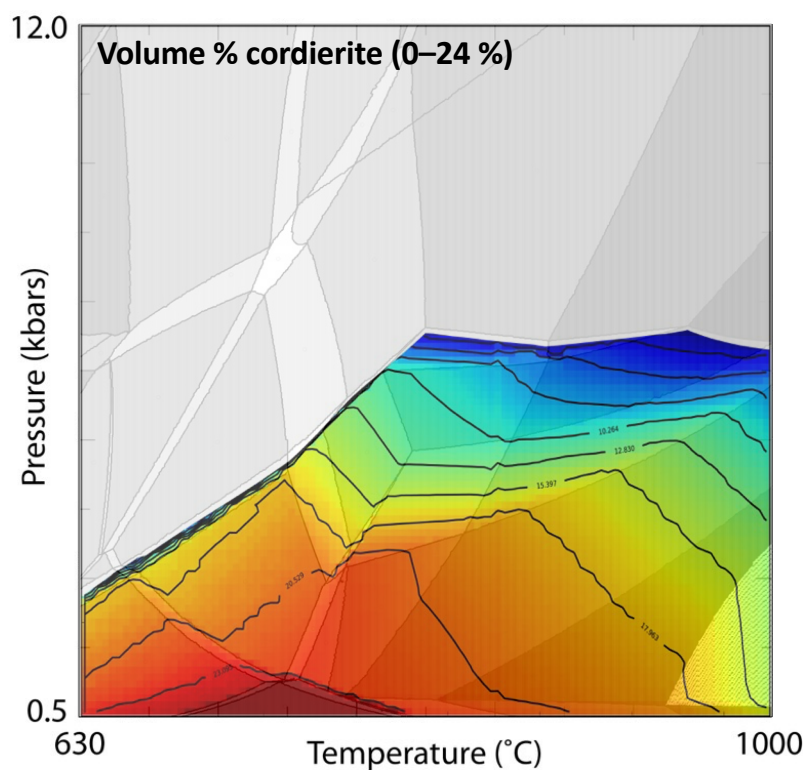**It's sometimes easier to set it running than it is to think...**

3 kJ/mol reduction to annite enthalpy

Phase abundances can be output as volume %, molar % or wt%, and can be output as a proportion of the system, or the system minus any accompanying fluid

Volume % melt (0–90 %)
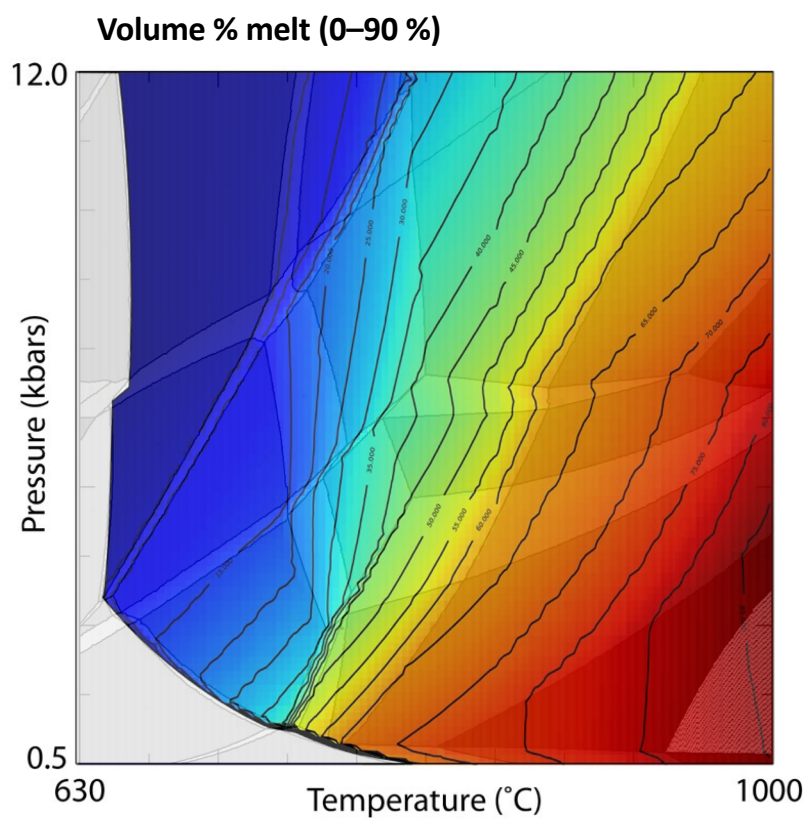
Contour plots or color maps almost always need tidying up in Illustrator or equivalent
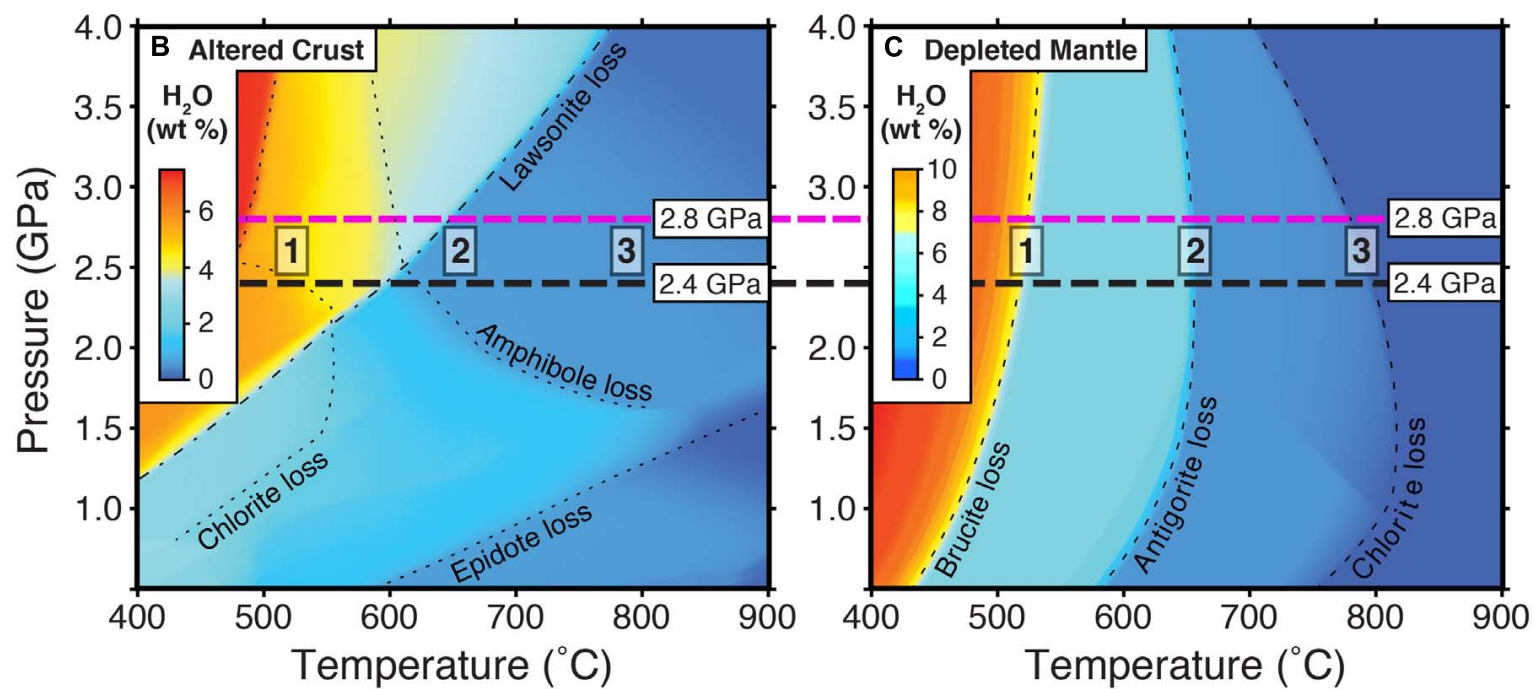
Wagner et al., (2020)

Phase fractionation

It is straightforward to progressively remove the compositions of phases that have been calculated as stable in previous steps.

This obviously implies a path dependency, so Perple_X needs to be given a *PT* path to work on

Phase fractionation

Any garnet and fluid calculated to be stable at a step were removed from the bulk-rock composition before successive steps

Caddick & Baxter (2013)

With no phases fractionated

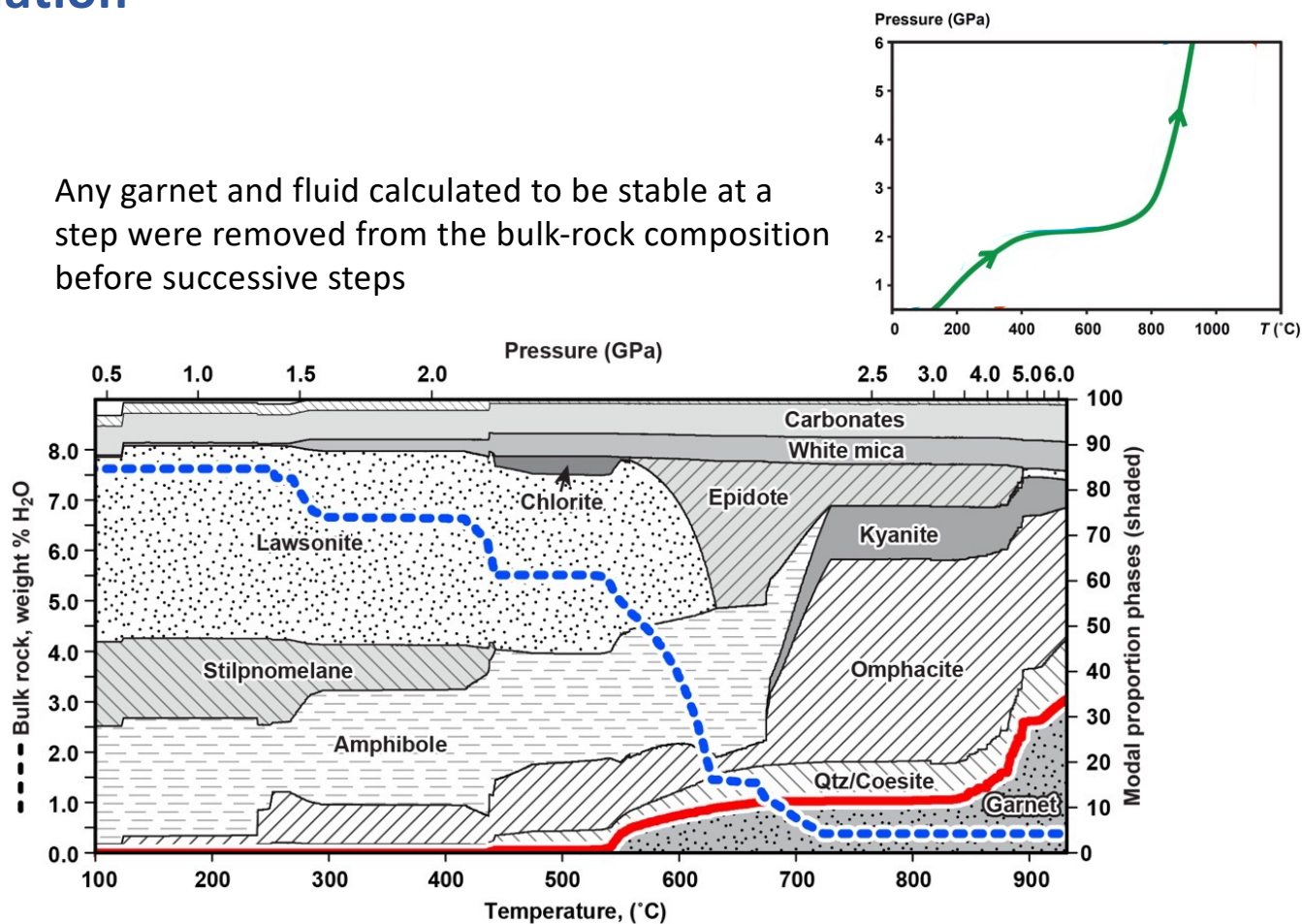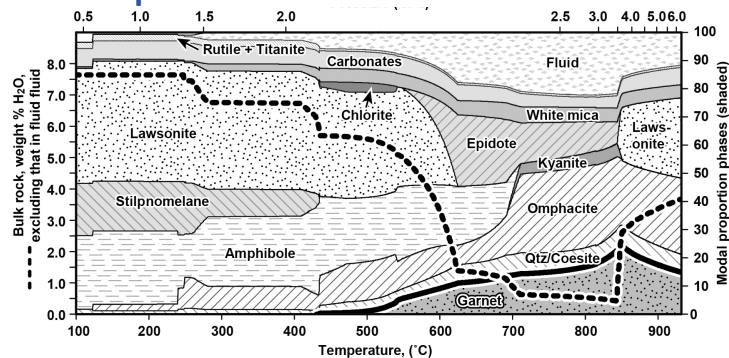**With just fluid fractionated**

Figure DR-3. Phase abundances calculated for a hydrated MORB on the Nicaragua geotherm. Calculations involve different assumptions: (a) garnet and fluid are progressively fractionated from the bulk rock composition as they form, (b) fluid is fractionated but garnet is not, (c) no phases are fractionated. Bold curves highlight garnet abundance (right-hand axis), bold dashed curves denote amount of bulk rock H₂O (excluding in fluid). Option (a) as in Figure 1c. Note that in (c) the persistence of a fluid phase could also lead to wet-melting

Caddick & Baxter (2013)

Perple_X Strengths and Weaknesses

Strengths:

Extremely flexible

Automatically finds the lowest free energy surface

Little chance of mistakenly calculating a meta-stable phase diagram… (but what if you want to do that)?

Requires almost no user input once the calculation parameters have been defined

Weaknesses:

Less useful as a pedagogical tool than 'by hand' calculation

Every end-member in your dataset of choice is considered (revealing areas of *PT* space in which their calibration 'fails')

Minimization can take many hours

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- Connolly JAD (2016) Liquid-vapor phase relations in the Si-O system: A calorically constrained van der Waals-type model. Journal of Geophysical Research-Planets 121:1641-1666 doi:10.1002/2016JE005059
- Helffrich G, Connolly JAD (2009) Physical contradictions and remedies using simple polythermal equations of state. American Mineralogist 94:1616-1619, doi:10.2138/am.2009.3262
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- Connolly JAD, Petrini K (2002) <u>An automated strategy for calculation of phase diagram sections and retrieval of rock properties as a function of physical conditions.</u> J Met Geol, 20:697-708. (<u>Errata</u>)
- Connolly JAD (1995) <u>Phase diagram methods for graphitic rocks and application to the system C-O-H-FeO-TiO2-SiO2</u>. Contrib Mineral Petrol 119:94-116
- Connolly JAD, Cesare B (1993) <u>C-O-H-S fluid composition and oxygen fugacity in graphitic metapelites</u>. J Metamorphic Geol 11:368-378
- Abart R, Connolly JAD, Trommsdorff V (1992) <u>Singular point analysis: construction of Schreinemakers projections for systems with a binary solution.</u> Am J Sci 292:778-805
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- Connolly JAD (1990) <u>Multivariable phase diagrams: an algorithm based on generalized thermodynamics</u>. Am J Sci 290:666-718
- Connolly JAD, Kerrick DM (1987) <u>An algorithm and computer program for calculating composition phase diagrams</u>. CALPHAD 11:1-55