about phase diagrams

- before starting to use THERMOCALC, we need to look at some general aspects relating to phase diagrams
- we will do this by thinking about a general model system (so, for example, KFMASH or NCKFMASHTO).

how to think about a model system

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- so we can only draw such diagrams for small and largely irrelevant systems (q-coes-trid-stis in SiO_2 and ky-sill-and in Al_2SiO5 are exceptions)
- so how do we proceed? By way of *sections* and *projections* of the information in the total phase diagram, aiming for useful 2D representations of the mineral equilibria.

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    - in pairs: $\{P, V\}$, $\{T, S\}$, $\{\mu_k, n_k\}$
- so there are actually many possible total phase diagrams for the one model system, in fact 2^n of them, depending on which variable in each pair is represented.

intensive variables

- e.g. P, T, μ_k

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- contact equilibrium
- equilibration by:
  $P \longrightarrow$ deformation; $T \longrightarrow$ conduction; $\mu_k \longrightarrow$ diffusion;

extensive variables

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- we usually deal with the extensive variables in normalised form, so X_k rather than n_k.

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- ...so, which energy minimised depends on the system
- from *our* perspective, if the intensive variable is superimposed on our system, then that is the "natural" one of the pair to be involved as an axis of our total phase diagram.

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- however, two recent papers to read regarding situations where the PTX world is inappropriate:
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    - Guiraud, M, & Powell, R, 2006. P-V-T relationships and mineral equilibria in inclusions in minerals. *Earth and Planetary Science Letters* **244**, 683–694.

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  - Guiraud, M, & Powell, R, 2006. P-V-T relationships and mineral equilibria in inclusions in minerals. *Earth and Planetary Science Letters* **244**, 683–694.
- in the PTX world, when a phase is considered to be “in excess” (e.g. $+$ H_2O fluid): this *can* (unwisely?) be considered in terms of a corresponding component being handled implicitly as a chemical potential. . .

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- representing mineral equilibria from the multi-dimensional total phase diagram in 2D is done with *sections* and *projections*
- an inevitable loss of information in each; often several different sections and projections needed
- need to be imaginative in order to show what needs to be shown (though PT pseudosections are indeed very powerful).

sections and projections

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- projections
- (pure) sections
- pseudosections

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  - main sort are PT projections
  - can show univariant (reaction) lines and invariant points
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  - T-X and P-X diagrams, with all other components being handled by phases in excess (impossible, normally)
- pseudosections
  - *pseudo* because they are at constant bulk composition, not at constant chemical potentials
  - very powerful diagrams for thinking about rocks.

variance

let's look at some calculated examples of these types of phase diagram, and see what is involved in calculating them with THERMOCALC. But, first, variance. . .

- $variance = c - p + 2$
- c = no of components; p = no of phases

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- so, for example, in an n-component system, n phases is divariant, and $n + 1$ is univariant,
- in larger systems, most equilibria have a variance larger than 2
- this is the usual definition of variance in the PTX world. . .

effective variance

when running THERMOCALC

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effective variance

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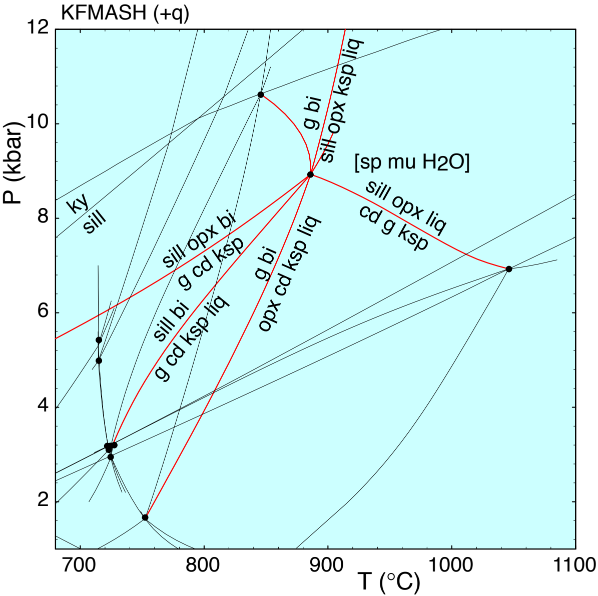
- variance, when prompted for, applies to the mineral equilibrium being considered, *prior* to applying constraints (like specifying a bulk composition)
- *effective variance* is what THERMOCALC recognises such constrained equilibria to be, and
- on a PT pseudosection, points are effective invariant, and lines are effective univariant.

PT projection



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- so reactions change continuously along lines
- and this is what makes them difficult to read to consider rocks (and why PT pseudosections are a powerful tool).

more features of PT projections

complexities

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complexities

- solvus relationships

more features of PT projections

complexities

- solvus relationships
- singularities, where phases change side along a reaction

  Worley, B, & Powell, R, 1998. Singularities in the system Na_2O–CaO–K_2O–MgO–FeO–Al_2O_3–SiO_2–H_2O. *Journal of Metamorphic Geology* **16**, 169–188.

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- relationships between sub-systems and the full system

  White, RW, Powell, R, & Clarke, GL, 2002. The interpretation of reaction textures in Fe-rich metapelitic granulites of the Musgrave Block, central Australia: Constraints from mineral equilibria calculations in the system K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O-TiO_2-Fe_2O_3. *Journal of Metamorphic Geology* **20**, 41–55.

  Yang, J-J, & Powell, R, Calculated phase relations for UHP eclogites and whiteschists in the system Na_2O-CaO-K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O. *Journal of Petrology*, in press

calculating PT projections

before we run THERMOCALC, note that

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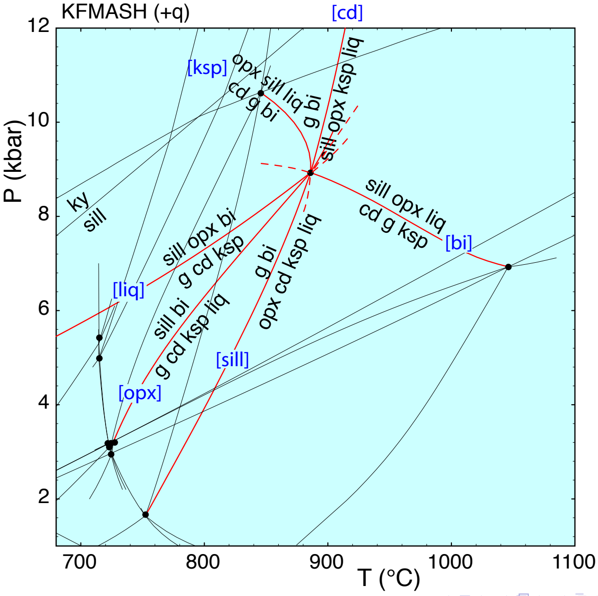
- if there is more than one rosette, the rosettes are combined manually, to determine their absolute stabilities
- see the documentation on the CD for details, and, if you are interested in learning more about this, do the auxiliary practical on the CD!

doing Schreinemakers



running THERMOCALC

- NASH (simple example with no solid solutions, so it is calculated in mode 3: THERMOCALC does the Schreinemakers for you)
- the staurolite isograd reaction in KFMASH (with solid solutions—Fe-Mg exchange and Tschermak's substitution—so it requires calculation in mode 1)

THERMOCALC datafile structure

- *a*-*x* relationships

  $*$

  scripts

  $*$

  storage

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- simplest example, for NASH calculations

  ab pa ky sill and q H2O

THERMOCALC datafile structure

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- simplest example, for NASH calculations

  ab pa ky sill and q H2O
- free format, but some things have to be on single lines
- will accept rationals in several situations (e.g. 1/2)
- lines beginning with a % are comment lines.

NASH reactions

```
Temperatures in the range 200 <-> 1000°C;  (for x(H2O) = 1.0)
uncertainties at or near 17.0 kbars

                           T°C   2.0   6.0  10.0  14.0  18.0  22.0  26.0     sdT  sdP
1)  and = ky                     352   680     +     +     +     +     +       6 0.068
2)  sill = ky                    435   623   806   984     +     +     +       5  0.11
3)  sill = and                   717   452   235     -     -     -     -      13  0.25
4)  jd + q = ab                    -     -   313   487   654   813   960       7  0.16
5)  pa + q = ab + ky + H2O       543   615   670   719   763   804   842       3  0.31
6)  pa + q = ab + and + H2O      521   623   714   800   883   966     +       3  0.14
7)  pa + q = ab + sill + H2O     527   616   693   764   831   895   958       3  0.16
8)  pa = jd + ky + H2O             +     +     +     +     +   779   536      20  0.27
9)  pa = jd + sill + H2O           +     +     +     +     +     +   954      11  0.54
```

NASH invariants

```
P-T of intersections(for x(H2O) = 1.0)
window : P 2.0 <-> 32.0 kbars; T 200 <-> 1000°C
in excess : q H2O

· stable intersection 1 involving ky,and,sill + (q,H2O)  or [pa,ab,jd]
                          low T  high T    dp/dt
3)  sill = and     [ky]          stable  -0.0154
1)  and = ky     [sill]  stable           0.0122
2)  sill = ky     [and]          stable   0.0214
P = 4.4 kbar (sd = 0.1), T = 550 °C (sd = 8), (cor = 0.802)

· stable intersection 2 involving pa,ab,jd,ky + (q,H2O)  or [and,sill]
                                       low T  high T    dp/dt
8)  pa = jd + ky + H2O          [ab]  stable          -0.0147
4)  jd + q = ab              [pa,ky]  stable stable    0.0259
5)  pa + q = ab + ky + H2O      [jd]  stable            0.100
P = 21.7 kbar (sd = 0.2), T = 800 °C (sd = 4), (cor = 0.667)
```

THERMOCALC datafile structure: *a*-*x* relationships

in *a*-*x* relationships for each phase, primary information is

- phase name
- variable names and *initial guesses*
- algebra for end-member proportions
- interaction energies
- algebra for site fractions
- algebra for ideal mixing activities (in terms of site fractions)

example: garnet

```
g 2
      x(g) 0.7

%-----------------------------

  p(py)    1 1      1  1 -1   x

  p(alm)   1 1      0  1  1   x

%-----------------------------
sf
  w(g) 2.5 0 0

%-----------------------------

2  x(Mg)   1 1      1  1 -1   x

   x(Fe)   1 1      0  1  1   x

%-----------------------------
     py      1  1    x(Mg)  3

     alm     1  1    x(Fe)  3
```

example: scripts

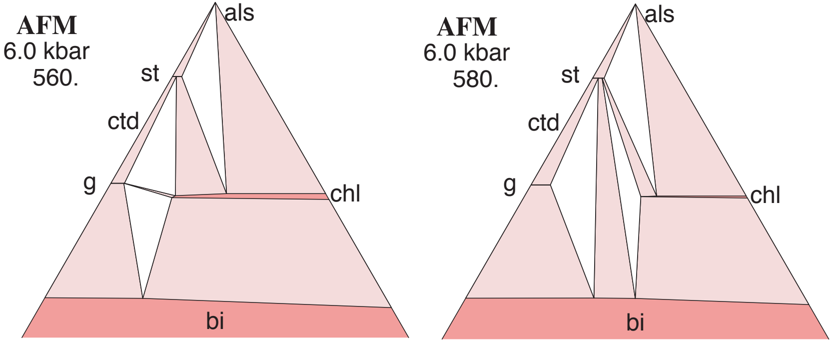
```
fluidpresent yes
fluidexcess yes
setexcess mu q

calctatp ask
setiso no

setdefTwindow yes  200 1100
setdefPwindow yes  0.1   15

project no
% ------------------------------------------------
%                        H2O  SiO2 Al2O3   MgO   FeO   K2O
setproject     A          0     0     1     0     0     0
setproject     F          0     0     0     0     1     0
setproject yes M          0     0     0     1     0     0
% ------------------------------------------------

pseudosection no
% ---------------------------------
% tutorial bulk: "average" pelite
% ---------------------------------
%           SiO2  Al2O3  MgO   FeO   K2O
setbulk yes  150  41.89 18.19 27.29 12.63
% ---------------------------------
```

staurolite isograd reaction

```
<====================================================>
phases : chl, bi, st, g, (mu, q, fluid)
 P(kbar)     T(°C)   x(chl)   y(chl)   Q(chl)    x(st)     x(g)     x(bi) etc
    5.00     537.5   0.8502   0.6586   0.3414   0.9779   0.9765   0.9074
        18chl + 39g + 68mu = 68bi + 10st + 133q + 54H2O
    6.00     560.3   0.6903   0.6138   0.3861   0.9444   0.9405   0.7639
        23chl + 30g + 65mu = 65bi + 10st + 115q + 74H2O
    7.00     576.9   0.5885   0.5929   0.4070   0.9144   0.9078   0.6469
        27chl + 24g + 63mu = 63bi + 10st + 100q + 87H2O
    8.00     590.4   0.5126   0.5798   0.4202   0.8852   0.8757   0.5581
        28chl + 21g + 61mu = 61bi + 10st + 92q + 94H2O
    9.00     602.2   0.4499   0.5701   0.4298   0.8550   0.8424   0.4898
        29chl + 19g + 61mu = 61bi + 10st + 89q + 96H2O
   10.00     613.1   0.3953   0.5626   0.4374   0.8229   0.8065   0.4343
        29chl + 19g + 61mu = 61bi + 10st + 88q + 96H2O
   11.00     623.3   0.3462   0.5564   0.4436   0.7881   0.7671   0.3867
        29chl + 19g + 61mu = 61bi + 10st + 89q + 96H2O
   12.00     633.2   0.3015   0.5512   0.4488   0.7501   0.7237   0.3439
        29chl + 20g + 61mu = 61bi + 10st + 91q + 95H2O
```

example compatibility diagram

KFMASH (+ q + mu + H2O)



features of compatibility diagrams

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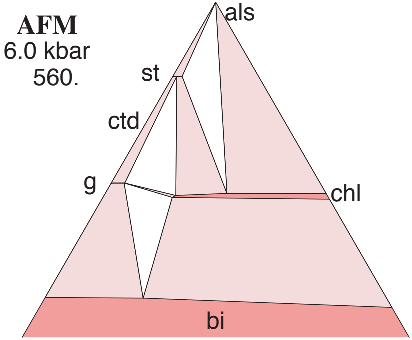
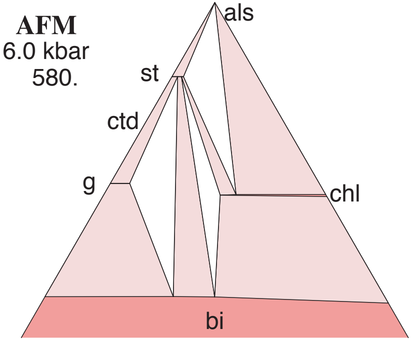
- tie lines join coexisting phases
- tie triangles are divariant, tie line bundles are trivariant, and one-phase fields are quadrivariant.

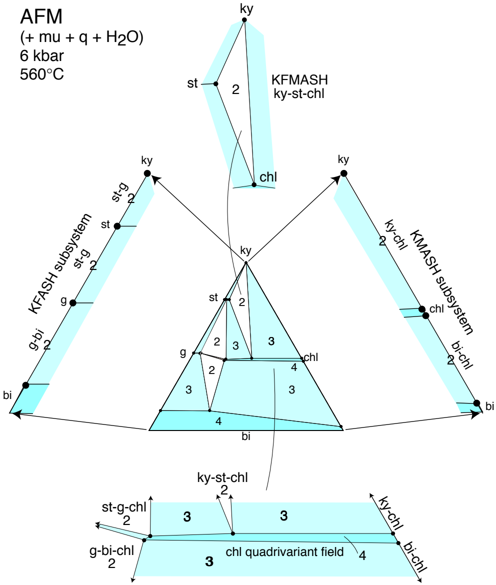
AFM compatibility diagrams

KFMASH (+ q + mu + H2O)





compatibility diagram construction



AFM
(+ mu + q + H_2O)
6 kbar
560°C

THERMOCALC

now let’s calculate an AFM tie triangle

AFM tie triangle info

```
project yes
% ------------------------------------------------
%                        H2O  SiO2 Al2O3   MgO   FeO   K2O
setproject     A          0     0     1     0     0     0
setproject     F          0     0     0     0     1     0
setproject yes M          0     0     0     1     0     0
% ------------------------------------------------
```

```
<==================================================>
phases : chl, bi, g, (mu, q, fluid)

 P(kbar)     T(°C)   x(chl)   y(chl)   Q(chl)    x(bi)    y(bi)    Q(bi) etc
    7.00     560.0   0.6947   0.5811   0.4189   0.7524   0.3497   0.1847

proj        A       F       M       q     H2O      mu    phase
chl     0.194   0.560   0.246   0.473   0.667              -0.167
bi     -0.272   0.961   0.311  -0.228            0.500   -0.500
g       0.250   0.707   0.043   0.750                      -0.250
```

more on compatibility diagrams

complexities

more on compatibility diagrams

complexities

- what phases to have “in excess”

more on compatibility diagrams

complexities

- what phases to have “in excess”
- choosing a compatibility diagram triangle

more on compatibility diagrams

complexities

- what phases to have “in excess”
- choosing a compatibility diagram triangle
- phases plotting at infinity.

compatibility diagram movie)

a movie. . .