

some notes on pseudosection calculations and dogmin in particular

The focus here is on generating a good starting point for calculating a pseudosection and also for checking the phase relations when a pseudosection is underway. The primary tool is dogmin, accessed by the script “dogmin”. Dogmin tells THERMOCALC to look at all the equilibria involving subsets of the phases given in the “with” script, from a user-provided maximum variance down to a minimum variance (by default, divariant), and THERMOCALC reports which has the lowest Gibbs energy¹. See “dogmin” in the script notes.

Dogmin, in using brute force, needs considerable care to be useful. It is not as simple as just throwing a large set of phases at it, and expecting it to give the right answer. Dogmin may give a plausible answer, but still may have missed calculating the equilibrium which has the lowest Gibbs energy. This is primarily because the capacity of THERMOCALC to calculate an equilibrium depends on how good are the starting guesses for the *xyz* variables in the equilibrium. In addition there are various other things that can go wrong. Starting guesses for the *xyz* variables in an equilibrium are communicated to THERMOCALC by the “xyzguess” script. In turn these are generated by THERMOCALC calculations with the information in “xyzguess” form given in the logfile. See “xyzguess” in the script notes.

Before starting, it is recommended to have a complete set of “xyzguess” blocks in the scriptfile, one for each of the phases in the “with” list of phases. Such blocks may be copied in from example information on the website, but of course with no guarantee that they are optimal for the present purpose. With this preliminary set of xyzguess blocks in place, the first thing needed is to boil down the composition dimensions in the axfile codings that are not needed. This is done by setting to zero the appropriate *xyz* variables in the blocks. For example if the bulk composition for the pseudosection does not include Mn, then the $m(\cdot)$ variables in the blocks should be set to zero. If the phases in the “with” list include ‘dependent’ phases from “samecoding” (e.g. paragonite, for “samecoding mu pa”), then an xyzguess block needs to be made for the ‘dependent’ phase from that of the ‘independent’ phase, changing the phase name to that of the ‘dependent’ phase. At least some of the values need to be different too, reflecting the fact that generally the ‘independent’ and ‘dependent’ phases are separated by a solvus. For example, for paragonite, the $n(\text{pa})$ might be made to be 0.95, and the $y(\text{pa})$ to be 0.98, so that paragonite is clearly on the other side of the muscovite-paragonite solvus.

Now to proceed, the idea being to replace the preliminary “xyzguess” blocks with ones that are the result of your calculations with your bulk composition. An hour or more of careful work at this stage will save much pain later, or the potential for such pain. This can be done

¹“Dogmin” = DO Gibbs energy MINimisation.

bootstrapping using “dogmin” itself.

Some things to do and not to do:

- run “dogmin” at just one P and one T using “dogmin 1”: the information provided by “dogmin” is more informative if the calculations are done at just one PT . The calculations are also safer given that one set of starting guesses may not be sufficient over a PT range. Also more phases may need to be included in the “with” list, making the dogmin runs longer.
- which PT ? One choice is your best guess of the PT of your rocks (or one of your rocks), then you already know what the core set of phases that are needed in the “with” list. Use the “calcP” and “calcT” scripts to set this PT .
- which phases to include in the “with” list? If you throw too many phases into the list, not only will THERMOCALC take a long time to do the calculations, but it can be difficult to appraise what THERMOCALC has done. It is better to start with a more limited set of phases, get good starting guesses for those, then incrementally increase the number of phases.

Getting the starting guesses involves looking at the information on screen (or at the bottom of the logfile) and also the block of information in the icfile. This information gives the cross-referencing, via the # number, to the calculations in the body of the logfile where the “xyzguess” blocks can be found.

Here is an example of the onscreen block of information²: assemblage modes for minimum G, and near minimum G, at $P = 7$ kbar and $T = 600^\circ\text{C}$

#	g	bi	st	chl	ctd	:	mu	q	H2O	G	odel	del
16	0.151	0.254	0.080	-	-	:	0.179	0.152	0.184	-793.33098	-	-
6	0.262	0.149	-	-	-	:	0.279	0.119	0.190	-793.32232	0.00866	0.00866
10	-	0.397	0.187	-	-	:	0.042	0.197	0.176	-793.32010	0.01088	0.00222
24	-	0.299	-	0.056	0.192	:	0.136	0.190	0.127	-793.17857	0.15241	0.14153
12	-	0.330	-	-	0.234	:	0.106	0.193	0.136	-793.17772	0.15326	0.00085
11	-	0.163	-	0.307	-	:	0.265	0.176	0.088	-793.16441	0.16657	0.01331
...												

In the logfile, these equilibria can be found via their # numbers, the minimum G assemblage being #16. The logfile contains all of the equilibria that calculated whether they are ‘seen’ by the bulk composition or not. The information in the icfile summarises this, the ‘—’ lines being calculated but not ‘seen’:

²This is for KFMASH calculations with mu, q and H₂O in excess, with a bulk, H₂O=25.4318, SiO₂=42.2270, Al₂O₃=11.3240, MgO=4.1906, FeO=13.7691, K₂O=3.0574

#	g	bi	st	chl	ctd	G
1	X	-	-	-	-	-793.03711
2	-	X	-	-	-	
3	-	-	X	-	-	
4	-	-	-	X	-	-793.00673
5	-	-	-	-	X	
6	X	X	-	-	-	-793.32232
7	X	-	X	-	-	---
8	X	-	-	X	-	-793.08710
9	X	-	-	-	X	---
10	-	X	X	-	-	-793.32010
11	-	X	-	X	-	-793.16441
12	-	X	-	-	X	-793.17772
13	-	-	X	X	-	---
14	-	-	X	-	X	
15	-	-	-	X	X	---
16	X	X	X	-	-	-793.33098
17	X	X	-	X	-	---
18	X	X	-	-	X	---
19	X	-	X	X	-	---
20	X	-	X	-	X	
21	X	-	-	X	X	---
22	-	X	X	X	-	---
23	-	X	X	-	X	
24	-	X	-	X	X	-793.17857
25	-	-	X	X	X	

Looking at #16 in the logfile, the starting guesses can be copied into the scriptfile, replacing the previous ones (which might be copied to beyond the * in the file in case they are needed later).

```
% ----- #16
xyzguess x(g)          0.887427
xyzguess z(g)          0 % boiler
xyzguess m(g)          0 % boiler
xyzguess f(g)          0 % boiler
xyzguess x(bi)        0.674182
xyzguess m(bi)          0 % boiler
xyzguess y(bi)        0.260333
xyzguess f(bi)          0 % boiler
xyzguess t(bi)          0 % boiler
xyzguess Q(bi)        0.0969282
% -----
xyzguess x(mu)        0.548754
xyzguess y(mu)        0.909621
xyzguess f(mu)          0 % boiler
xyzguess n(mu)          0 % boiler
xyzguess c(mu)          0 % boiler
% -----
xyzguess x(st)        0.858563
xyzguess m(st)          0 % boiler
xyzguess f(st)          0 % boiler
xyzguess t(st)          0 % boiler
% -----
```

Then #21 can be used to get the additional starting guesses for chlorite and chloritoid.

```
% ----- #21
xyzguess x(chl)      0.465451
xyzguess y(chl)      0.805095
xyzguess f(chl)      0 % boiler
xyzguess m(chl)      0 % boiler
xyzguess QA1(chl)    0.194402 range -1.000 1.000
xyzguess Q1(chl)     0.0352754 range -1.000 1.000
xyzguess Q4(chl)     0.0888073 range -1.000 1.000
% -----
xyzguess x(ctd)      0.772861
xyzguess m(ctd)      0 % boiler
xyzguess f(ctd)      0 % boiler
% -----
```

The original starting guesses that were used in the calculations above were from the $g + chl = bi + st$ univariant, with a (poor) ctd guess. Using the upgraded starting guesses allowed one more equilibrium to be calculated, #20. The worse the initial starting guesses the more equilibria will be able to be calculated with upgraded starting guesses. The table of diagnostic information at the top of the icfile may help identify equilibria that might have been expected to be calculated, but have not been. This may flag starting guess problems.

- what range of variance should be examined, as specified by “maxvar” (see the script notes)? If there are c oxides in the bulk composition, the actual maximum variance is $c - 1$, for example for conditions above the liquidus where just the one phase is stable. But generally this number is unnecessarily large. For AFM at lower temperatures chlorite plus the in excess phases is commonly the stable assemblage, and in this case, with $c = 6$, the maximum variance to use would be 4. In smaller systems the default minimum variance of divariant will be appropriate. For larger systems, say with $c > 9$, THERMOCALC effort is reduced by making the minimum variance 4 or 5.
- whether to involve in excess phases? Given that the phases in the “inexcess” script have to be included in all the equilibria calculated, this is a good way of reducing the length of dogmin runs. But just because a phase is in the “inexcess” list does not mean that the phase will occur in the chosen bulk composition. So care is required. Best to start without in excess phases, unless the rock is obviously quartz-rich, say, then having in excess quartz make sense. When calculations are underway, the dogmin info as in the table on page 2 can be appraised. All the assemblages involve biotite so biotite is a candidate for the “inexcess” list. Small modes of in excess phases in such a table might flag whether phases chosen to be in excess may not be present in all relevant equilibria. Of course it is easy to do a run with and a run without the in excess phases and look for differences that may flag an inappropriate choice of in excess phases.

Particular care is needed with calculations intended to be H₂O-saturated—so H₂O should be in the “inexcess” list—that enough H₂O has been added into the bulk composition for the relevant equilibria to be calculated. The H₂O-content of, for example, chlorite is high, so more H₂O is needed in the bulk to accommodate chlorite-bearing equilibria.

- care with samecoding phases³! The problem here is that the samecoding phases are separated by solvi, at least if the calculation conditions are below the conditions of the solvus tops. For example, if you are doing calculations that involve *any* of the phase in “samecoding hb act gl cumm”, and you have put actinolite in your “with” list, then just because THERMOCALC says that an assemblage has calculated an actinolite-bearing assemblage, there is no guarantee that THERMOCALC has not ‘jumped’ a solvus and calculated a hornblende, not an actinolite. So you need to look at the compositions of such phases to make sure that this has not happened. If it has happened, it may in fact say something useful about the mineral stabilities.

The ‘jumping’ problem is exacerbated if an equilibrium involves two phases from the same “samecoding” list, as both phases can end up with the same composition, one of the phases having ‘jumped’ the solvus between them. When calculations involve samecoding phases, the “xyzguess” information may need to be adjusted to help THERMOCALC calculate the equilibria. In general, calculations are more successful if the “xyzguess” information lies outside the solvus, rather than inside the solvus, in terms of the main composition variable or variables that define the solvus.

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³the same care is needed for normal THERMOCALC calculations, not just dogmin ones