

THERMOCALC Short Course (São Paulo): 2006

Day 2 Practical: \overline{PT}

The purpose of this practical is to understand more about \overline{PT} , following on from the lectures. This will be done using the Proyer example, following on from the first prac, and a lower amphibolite facies calc-pelite from the Dalradian of Scotland (the infamous RP13).

1. The full assemblage of the Proyer eclogite is garnet-omphacite-muscovite-talc-kyanite-quartz, unusually it is relatively low variance compared with many eclogites. This makes it a good candidate for success with \overline{PT} (more phases means more independent reactions and therefore the potential for better constrained PT). The number of independent reactions is equal to the number of end-members of phases minus the number of system components.

- (a) We will start by looking at the mineral assemblage using the omphacite as analysed (so with $x(\text{cpx}) = 0.216$), even though we know from the last prac that it causes very high temperatures for the g-cpx Fe-Mg exchange thermometer. Run THERMOCALC with datafile `tcdproyer3.txt` for \overline{P} over the T range 600° to 1000° , using a P interval like 10 to 50 kbar (large enough to be fairly sure of capturing the positions of the reactions). It is always best to start with \overline{P} , rather than jump straight in with \overline{PT} as the latter may not give helpful results (see below).

Look at the results: we can see that sigfit (ie σ_{fit}) is OK at lower T , so rerun \overline{P} over the T range 600° to 700° . That there is a minimum in σ_{fit} suggests that \overline{PT} would work well, so we run that next. Make a note of the \overline{PT} result and uncertainties for reference to results obtained below. (Note that the T is low compared with the g-cpx T from the first prac with $x(\text{cpx}) = 0.216$. Why?)

Looking at the diagnostics, σ_{fit} just about passes the χ^2 test, so there is no justification for omitting end-members from the calculation. however note that all of σ_T , σ_P and σ_{fit} are all decreased substantially by doubling the activity uncertainty of hedenbergite, and the residual is large. (This is hardly surprising as hedenbergite is the end-member most affected by erroneously assigning $\text{Fe}^{3+} = 0$)

- (b) Now look at the mineral assemblage using the omphacite as analysed, but with the Mössbauer Fe^{3+} value (so with $x(\text{cpx}) = 0.112$). So change the value in `tcdproyer3.txt`, and rerun THERMOCALC. What has changed? Is this better?

Note that the hat value of pyrope is large, meaning that to an extent the result is controlled by this value. Although there is no good reason to leave it out, what is the effect of omitting it? Is the result within $\pm = 2.5\sigma$ of the previous result? What has happened to the uncertainties on the results? What does this say for the significance of pyrope in the calculation?

- (c) A variable additional to PT is $a_{\text{H}_2\text{O}}$: it has been assumed in the above calculations that the rock was H_2O -present during development of the mineral assemblage (meaning that $a_{\text{H}_2\text{O}} = 1$). At these high pressures, some argue that the fluid, if present, may well contain lots of goodies (e.g. alkalis) and these will lower the $a_{\text{H}_2\text{O}}$. The first approach is to leave out H_2O from the calculation altogether (try this); the second is to run the calculation at a series of lower $a_{\text{H}_2\text{O}}$ values (say 0.5 and 0.2). Try this too: you are able to put a water activity in if you answer no to the question “rock was fluid-bearing ?” (this covers the H_2O -diluted-by-something case as well as the H_2O fluid-absent one)
- (d) Draw the uncertainty ellipse (using $\pm = 2.5\sigma$) for this eclogite (for H_2O -present) on a PT diagram, 500 to 750°C and 15 to 40 kbar. Show also the trace of \overline{P} and its uncertainty band (using $\pm = 2\sigma$: why is this 2-times when the ellipse is 2.5-times?).

2. RP13 is a lower amphibolite facies calc-pelite from Spean Bridge in the Dalradian of the Scottish Highlands, that involves the relatively low-variance assemblage quartz-oligoclase-muscovite-biotite-chlorite-garnet-epidote-calcite. The activities of the end-members of the minerals in `tcdrp13.txt` were generated from mineral analyses by AX; the uncertainties are the default ones of Powell and Holland (1988), obtained by the script, `usedefsda`. (So this is an “old-fashioned” style of datafile).

It is reasonable to assume that the rock was fluid-present during development of the mineral assemblage. The conditions of formation therefore include P , T and the composition of the metamorphic fluid. If it is assumed that the fluid was dominated by H_2O and CO_2 , then there is one fluid composition variable, say, x_{CO_2} (with $x_{\text{H}_2\text{O}} = 1 - x_{\text{CO}_2}$)

- (a) First of all run THERMOCALC with the data as it is in the datafile, for a T range of 450 to 650°C at a starting “guess” of $x_{\text{CO}_2} = 0.25$. Not a good result: σ_{fit} fails badly. Look carefully at all the diagnostics and identify the obvious culprit.

Plot the columns of the diagnostic, y against x , these representing the respective contributions of the end-members to the \overline{P} result. The \overline{P} least squares process amounts to drawing the best fit line through the points *and* the origin (i.e. the $\{0,0\}$ point of the plot. Draw what you think is the best line and work out its slope. This slope *is* \overline{P} . Observe that the discrepant end-member lies well off your line, and also observe that the data with high hat values plot far from the origin, effectively fixing the slope of the line.

- (b) Remove the “bad” outlier and rerun THERMOCALC at $x_{\text{CO}_2} = 0.25$: the quality of the result is now good. (The bad datum is the activity of paragonite—hopefully you got this!—it actually should not have been included as it is the end-member associated with the “other” side of the muscovite-poaragonite solvus).

- (c) Now think about how to proceed? At least at $x_{\text{CO}_2} = 0.25$, we have a good result. How should we investigate the dependence of the result on fluid composition? The first option is to treat the fluid composition as a “nuisance” parameter: we rerun THERMOCALC leaving out H_2O and CO_2 (try this). This should work, so now run an \overline{PT} . Is this result useful?

The next option is to run \overline{PT} at a series of x_{CO_2} . The “best” fluid composition (and PT) will correspond to the overall minimum in σ_{fit} .

- (d) Give your preferred estimate of the PT of this rock, and the likely range of x_{CO_2} , using the idea that you want σ_{fit} to be less than the χ^2 limit (in this case $\sigma_{\text{fit}} < 1.4$), quoting the \pm on the PT as 2.5σ .
- (e) As an afterthought, see what the garnet-biotite Fe-Mg thermometer gives at the preferred P , for this rock, looking particularly at the \pm_T .