

Although little time will be spent on thermometry and barometry in the course, the average  $PT$  approach to thermometry and barometry is covered in the following papers

- Powell, R, and Holland, TJB, 1988 An internally consistent thermodynamic dataset with uncertainties and correlations: 3: application methods, worked examples and a computer program. *Journal of Metamorphic Geology* **6**, 173-204.
- Powell, R, and Holland, TJB, 1994. Optimal geothermometry and geobarometry. *American Mineralogist* **79**, 120-133.
- Worley, B, and Powell, R, 1999. High-precision relative thermobarometry: theory and a worked example *Journal of Metamorphic Geology* **18**, 91-102.

The main idea involved in the average  $PT$  approach to geothermometry/barometry is summarised in the abstract to Powell & Holland (1994):

With the existence of thermodynamic data for a wide range of end-members in rock-forming minerals, thermobarometry now involves combining many equilibria to find the  $PT$  of formation of a rock. We reiterate that this task need only involve an independent set of reactions representing all these equilibria. In finding a  $PT$  of formation, there is an implied displacement of the equilibria to coincide with this  $PT$ . These displacements are mainly made by varying the activities of the end-members of the minerals, in proportion to their uncertainties. As a consequence, the equilibria are constrained to move in a more or less highly correlated way because the equilibria involve *overlapping* subsets of the end-members. These essential correlations should be included in any thermobarometry calculations. Of the three thermobarometry approaches in use, the TWEEQU approach of Berman (1991), the individual species approach of Gordon (1992), and our average  $PT$  approach, only the last two are optimal on this basis. In addition, such optimal approaches allow  $PT$ , their uncertainties, and a range of diagnostics for outlier identification, to be calculated in a computationally inexpensive way.

Little has changed in the implementation of average  $PT$  in THERMOCALC since that paper was written. The only advance that has been made, extending the approach, is the  $\Delta PT$  one

# Delta $PT$ documentation

Apart from in the form of Mathematica functions (in the “math” folder), the  $\Delta PT$  approach of the last paper is not currently implemented, though the *plan* is to hive off av $PT$  from THERMOCALC, incorporate AX, and include  $\Delta PT$  in new software (to be called OPTIMUMPT?).

The following is a minimal edit of Brenton Worley’s  $\Delta PT$  documentation, to be consistent with its inclusion here.

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## Capabilities

Using the code in DELPT.NB it is possible to calculate differences in  $P$  and  $T$  between two samples with identical mineral assemblages (or sub-assemblages). The  $\Delta PT$  calculations can be based on either the av $PT$  or av $P$  methods, or the simultaneous solution of a geothermometer (garnet-biotite) and geobarometer (GASP).

It is also possible to calculate differences in  $P$  and  $T$  where the two assemblages vary by non solid-solution phases. For example two meta-pelitic assemblages in which the aluminosilicate is different, ie:

ky + g + bi + mu + plag + q

and

sill + g + bi + mu + plag + q

At this stage it is only possible to use fluid-conserved equilibria. Assemblages containing the following solid solution phases can be handled at present: muscovite, biotite, garnet, plagioclase, alkali feldspar, cordierite staurolite, orthopyroxene.

## The Mathematica Notebook

The cells of the Mathematica notebook (DELPT.NB) are grouped under four headings:

### General functions

The first group of cells (“General functions”) contains all of the code to perform the  $\Delta PT$  calculations. This block of cells, must be activated before calculations may be performed.

### Analyses

The cell titled Analyses is where the user inputs the mineral analyses. An example of mineral analyses, in terms of wt% oxides, for two assemblages is already in this cell. The general form for input is:

```
PHASE[iden] ^= {"SiO2","TiO2","Al2O3","FeO","MnO","MgO","CaO","Na2O","K2O"};
```

It is important that the name of the phase is in upper case, ie. MU, BI etc. "iden" refers to your identifier for the assemblage, clearly this will be different for each sample. The values for each oxide must be separated by a comma.

## Setup

Before  $\Delta PT$  calculations can be performed it is necessary to calculate an independent set of reactions for the end-members for your assemblages and linearise the thermodynamic data for these reactions within the PT window of interest.

These tasks are performed using THERMOCALC, and the resulting output is placed in the "Setup" cells. The precise setup info will depend on whether the user wishes to perform calculations on identical assemblages, or if it is necessary to look at the situation where a non solid solution phase is different between the assemblages (see earlier comment about the capabilities of the DeltaPT code).

**Same assemblage:**  $\Delta PT$  code requires

1. A vector of the end-member names
2. The reaction coefficient matrix for the independent set of reactions
3. The linearised thermodynamic data for each of the independent reactions
4. The covariance matrix for the "a" terms of the linearised thermo-data.
5. Some input/output identifiers.

Items 2-4 can be obtained by running THERMOCALC through an  $avPT$  calculation for a data file containing the end-members of interest. To get the relevant info it is necessary to "turn on" the script "makeinfo" in the data file, ie. enter "makeinfo yes" after the first asterix in your datafile (see "th dDeltaPT"). The info is then output in the "th math" file. Copy it from here into the Mathematica file.

It is necessary to change "a" to "aa", compare the Setup example to the output in the "th math" file. The vector of end-member names can also be constructed from the "th math" output.

The extra input/output info is of the form (see the example in the Setup cell):

```
Clear[MU]; Clear[Bi]; Clear[G]; Clear[PLAG];
ssphases = {MU,Bi,G,PLAG};
nssphases = {q,ky};

setup = {name, r, aa, b, c, cova, ssphases, nssphases};
```

The `Clear[PHASE]`, commands make sure that there are no pre-existing definitions for these names, you need one of these for each solid solution phase. "ssphases" is short for the list of solid-solution phases. "nssphases" is short for the list of non solid-solution phases (as these are equivalent to end-members, they are in lower case). "setup" just summarises the crucial information from this cell.

Note: it is critical that the order of the end-members in the vector "name" equates to the order of the phases in the vectors "ssphases" and "nssphases".

**Different assemblages:** If the two assemblages of interest differ by a non solid-solution phase, it is still possible to calculate the difference in  $P$  and  $T$ . However, the "setup" is slightly more complicated. In this situation you need to follow the above setup procedure for both assemblages. It is also necessary to calculate the covariance matrix for the enthalpies of formation of all of the end-members in the two assemblages. To do this just create a THERMOCALC data file which contains the name of all of the end-members. In the example given, the difference between the two samples is kyanite versus sillimanite. Therefore just add "sill" to the "th dDelta" datafile, "turn on" the "printcov" script, ie. type "printcov yes" and run THERMOCALC in mode 0. The covariance matrix is then output in the "th math" file. Note you do not need "G tables" or "H2O and CO2 fugacity tables or volume tables", so just type "no" or "0" when prompted for these.

The covariance matrix for the enthalpies "vhfull" and a vector of all of the end-member names "endmembers" should be put in the "Setup".

## Calculations

There are examples of calculations for both identical and different mineral assemblages. Calculating an  $avPT$  or  $avP$  simply requires calling the appropriate function:

```
avPTfull[iden,t,p,setup] or avPfull[iden,t#1,t#2,p,setup]
```

Full descriptions of the arguments passed to these functions is given in the Mathematical notebook.

Calculation of  $\Delta PT$  and  $\Delta P$  again requires calling one of the following functions:

```
deltaPT[iden#1,iden#2,minerals,t,p,setup] or
```

```
deltaP[iden#1,iden#2,minerals,t#1,t#2,p,setup]
```

The functions for calculating  $\Delta PT$  and  $\Delta P$  for different assemblages are only slightly different, in that two different "setup" summaries are required:

```
deltaPTd[iden#1,iden#2,minerals,t,p,setup#1,setup#2] or
```

```
deltaPd[iden#1,iden#2,minerals,t#1,t#2,p,setup#1,setup#2]
```

As usual there is no substitute for having a go!