Calculating pressures and temperatures of petrologic events: geothermobarometry

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The goal of this exercise is to calculate the pressure (P) – temperature (T) conditions at which two metamorphic rocks equilibrated, and to infer P-T paths that the rocks may have followed. You will calculate pressures and temperatures for two rocks from different regions of a metamorphic complex and compare/interpret the results.

The basic input of these calculations is the composition of minerals coexisting in equilibrium. Before carrying out the calculations, you must determine which minerals (and therefore compositions) to use, and you need to make observations of the minerals and their textures in thin section to guide the calculations and interpret the results.

In Part 1 of this exercise, you will lay the groundwork for the calculations. This preliminary work is essential in order to obtain geologically meaningful results (not just random numbers). In Part 2, you will carry out the pressure and temperature calculations, and in Part 3 you will consider ways to infer at least part of the pressure-temperature *path* that each rock followed during metamorphism and cooling/return to the Earth's surface (where the sample was collected).

PART 1

Samples X and Y are both garnet-bearing schists. The accompanying map shows the sample locations and geologic setting of these schists.

1. Briefly describe the location and setting of the samples using information from the maps and cross section. Relevant information should include: general location of the samples (which country/state/mountain belt? etc.), map distance of the samples from each other, types of structures and rock types present, and ages of rocks.

2. Examine one or more thin sections of each sample and do a complete petrographic description of the major minerals, their abundance, and textures. For each sample, make a representative sketch of a garnet showing its texture in relation to minerals near it. Don't forget to include a scale.

3. Describe (in words) the metamorphic grade of each rock, based entirely on your interpretation of the mineral assemblages. The rocks may have similar or different metamorphic grades, so treat each sample separately. Use the terms low, medium, or high grade to describe each sample, and give your evidence.

- How else can you describe the approximate metamorphic grade of each rock? (think about other methods/concepts you have used in this class).

- On the blank P-T diagram attached, outline the region(s) of P-T space at which you *estimate* Sample X and Sample Y equilibrated. Clearly label your diagram so that it is clear what your estimate for each sample is.

4. Examine the phase diagram provided by your instructor. This phase diagram shows the pressure and temperature positions of reactions (equilibria) that might have occurred in these rock samples. This phase diagram was calculated using the thermodynamic properties of the minerals and the assumption that all minerals are pure end-member phases (no solid solution). For minerals containing Fe, this means that no Mg substitutes for the Fe, even though in the real rocks, there is certainly some Mg. This assumption of pure phases means that this diagram may not be the best representation of the conditions experienced by the samples you are studying.

a. Think about which minerals in each samples are pure (no solid solution) and which are solid solutions. For solid solution phases, also list the **elements** involved, and the **name** of each solid solution end member. For example, if a sample contains olivine, you would write under the solid solution column:

olivine
 Fe (fayalite)
 Mg (forsterite)

SAMPLE X		SAMPLE Y	
pure minerals	solid solution minerals	pure minerals	solid solution minerals

b. Use the P-T diagram to determine which coexisting minerals in the rocks can be used to evaluate (calculate) temperature and which for pressure. *Recall that assemblages that make good thermometers have minerals with compositions (relative to each other) that are sensitive to temperature but not pressure,* and *barometers are assemblages whose relative mineral compositions are sensitive to pressure but not temperature.*

Fill in the chart:

SAMPLE X		SAMPLE Y	
thermometer minerals	barometer minerals	thermometer minerals	barometer minerals

5. You are not done looking at the rocks! Even though you now know what minerals you will use in your P and T calculations, and could go ahead and do the calculations based on knowing the compositions of the minerals, take a few minutes to look at the thin sections again. Things to observe and think about:

• Are all the minerals in your thermometry and barometry assemblages in contact (touching each other)? What do the contact areas (grain boundaries) look like? Think more about the issues of disequilibrium/equilibrium, and see if you are convinced that the minerals of interest represent an equilibrium assemblage.

The rest of the exercise will be distributed once Part 1 is completed.

PART 2

Once you have established which mineral assemblages and which mineral compositions will be used to determine temperature and which for pressure, you need to know the composition of each mineral that exhibits solid solution. A table of mineral composition data for both samples.

It is the composition of each **solid solution** mineral that is used in the thermometry or barometry calculation. Pure minerals are no longer considered: they must be present (for the reaction/equilibrium to occur), but we don't use compositional information from them in the calculations.

Using the mineral composition information in the accompanying table, you will compute metamorphic temperature and pressure for each sample.

** These data are listed as weight % oxides. You need to convert these data into **cations**. **

	Mineral compositions for Sample X				Mineral compositions for Sample Y		
	Garnet	Biotite	Plag		Garnet	Biotite	Plag
SiO_2	37.41	35.17	60.52	SiO_2	38.11	35.94	61.60
TiO_2	0.00	3.38	--	TiO_2	0.06	3.43	--
Al_2O_3	21.19	19.98	25.85	Al_2O_3	21.48	19.57	24.73
FeO	35.50	21.20	0.38	FeO	31.30	21.31	0.17
MnO	1.02	0.00	--	MnO	0.37	0.14	--
MgO	3.48	7.72	--	MgO	5.00	7.59	--
CaO	1.45	0.00	6.22	CaO	4.04	0.08	5.38
Na_2O	--	0.23	7.70	Na_2O	--	0.19	8.40
K_2O	--	9.81	0.05	K_2O	--	9.65	0.23
Total	100.05	97.49	100.73	Total	100.36	97.90	100.51

Minerals are not zoned in these samples

Additional mineral compositions for Sample Y

	Cordierite	Muscovite	Ilmenite
SiO_2	48.72	46.04	--
TiO_2	--	0.15	52.07
Al_2O_3	34.33	37.57	0.00
FeO	6.53	0.71	45.35
MnO	0.24	0.00	2.09
MgO	8.71	0.47	0.07
CaO	--	0.01	0.00
Na_2O	--	0.46	--
K_2O	--	10.85	--
Total	98.54	96.26	99.63

Follow the procedure outlined in the following pages for calculation of pressure and temperature.

Calculating pressures and temperatures with Kohn & Spear's GTB program
http://ees2.geo.rpi.edu/MetaPetaRen/Frame_software.html (with detailed instructions).

1. Start the program. The program can be run interactively (**cation** data are input from the keyboard) or the program can read a file of mineral compositions (**cations**; follow the instructions carefully for setting up this file). The main menu looks like this:

```
Program Thermobarometry
    COMMAND LEVEL

0 = EXIT
1 = Read Mineral File
2 = Make a new plot
3 = Plot Keq Lines on P-T Diagram
4 = Save Postscript file
5 = I/O switch (file or keyboard)
6 = Plot digitized reaction curves
```

2. If you have set up a file with cation data, choose option 1: read mineral file
(make sure you have set the I/O – input/output – switch in option 5 to your desired setting)

3. Guide the program to your file. After your file has been successfully read, choose Option 2 from the main menu and set the plotting parameters. Make sure the graph axes extend from 400-1000°C and 0-15 kbar. Decide if you want to save results as a PostScript file, and select the option for including an Al_2SiO_5 diagram in your P-T graph (for reference).

4. Then choose option 3; this performs the actual calculations. First find the thermometer you wish to use. If you are given more than one option for calibrations of this thermometer, select the first one in the list. Answer *no* to the question about whether to correct for Fe^{3+}.

5. Now you will be asked to input your data or to select the analysis from the table you created. The calculated temperatures are listed on the screen, and a line will be plotted on the graphics screen.

6. Now return to the Reaction menu (type 0), and switch to the geobarometry menu (type -1). Select your geobarometer(s) and plot the results on the same diagram as your thermometry result. Everything you do in a single session is plotted on one graph.

7. Repeat the above for the second sample. If you do calculations for both samples in one run (without quitting the program in between), keep track of which lines correspond to which sample.

8. Follow the instructions in the manual for capturing the image of the P-T diagram and/or other parts of the screen showing the results of your calculation; you may want to clean the image up in a graphic program, or you can annotate a printout to distinguish results from each sample.
Print a P-T diagram showing your thermometry and barometry results for Samples X and Y. Clearly label which results correspond to which sample.

PART 3

The temperature and pressure that you have calculated may represent the conditions at or near the peak of metamorphism: the highest temperature (and the pressure corresponding to the highest temperature) experience by the rock (be sure that you know why this is likely to be the case).

- Is there any way to determine the conditions the rock experienced on its way to the peak? and/or the post-peak conditions?

Look at the samples again and think about what you know about the history of each rock. For example, consider:

- Where was the rock prior to metamorphism? (think about the protolith of the rock)
- Where is the rock now?

Is there any other evidence from Sample X or Y (or neighboring rocks) that can be used to infer more about the path? If so, describe/discuss, and add the information to your P-T diagram. Be sure that everything on your diagram is well labeled (estimated conditions, calculated conditions, completely guessed at conditions, etc.).

Alternative modules

Calculating pressures and temperatures with Berman's TWQ program (requires DOS)
(see detailed instructions for running the software, included with this exercise)

Using the mineral composition information in the Table provided, calculate a new P-T diagram for each sample: one that is based on the actual mineral compositions in the rocks. Follow these steps to create the diagrams:

1. See the accompanying chart of mineral compositions, and edit the file rock.cmp with the MOLE FRACTIONS of each end member phase in your thermometer and barometer assemblages. Note that the names of the end member phases are abbreviated; e.g., ALM = almandine. I recommend that you rename the files (put the sample names in each) to something distinctive; also include your initials if you are sharing a computer.

2. Start up the TWQ program as before, input the relevant elements (include H_2O if there are hydrous phases), limit your diagrams to 0-900° C and 0-12000 bars, and select the phases of interest from the table displayed. Work on Sample X first.

3. After you do the phase selection step, tell the program to read your edited rock.cmp file. When the program asks you questions about particular calculation models (e.g., McMullen et al. 1990), accept all defaults.

4. Examine and print the resulting P-T diagram.

- What T (or range of T's) is indicated by your thermometer?
- What P (or range of P's) is indicated by your thermometer?
- At what conditions do your thermometer(s) and barometer(s) intersect?

5. Using the P-T diagram from Part 1, question #2, add your calculated P-T result to the diagram Discuss the correspondence or lack thereof of your calculated and estimated results.

6. Repeat for Sample Y.

Calculating pressures and temperatures with P, T equations

Geothermometry: Fe-Mg exchange between garnet and biotite

The ratio of Fe to Mg in garnet and biotite is a function of the temperature at which the minerals last equilibrated (interpreted to be at or near the peak temperature).

The first experimental calibration of the thermometer was done by Ferry & Spear (1978). They did a series of experiments at 2 kbar and a range of temperatures with garnet and biotite of different compositions.

The partitioning of Fe and Mg between garnet and biotite can be expressed by the parameter K_D:

$$\text{where } K_D = \left(\frac{X_{Mg}^{grt} X_{Fe}^{bt}}{X_{Fe}^{grt} X_{Mg}^{bt}} \right),$$

which can also be expressed as
$$K = (Mg/Fe)Gt / (Mg/Fe)Bt$$

1a. Using the data in the table below, make a graph of lnK (natural log of K) vs. 1/T in Kelvin (the inverse of temperature expressed in degrees Kelvin).

Mg/Fe Gt	Mg/Fe Bt	T C
0.105	0.333	799
0.116	0.408	799
0.116	0.439	749
0.104	0.370	738
0.110	0.420	698
0.116	0.449	698
0.110	0.473	651
0.115	0.513	651
0.109	0.550	599
0.114	0.639	599
0.107	0.613	550
0.114	0.695	550

b. Draw a line through the data. I recommend that you use a plotting program to draw a best fit line (linear regression). **Print this plot and your calculations of lnK and 1/T.**

2. Now determine a value of K for each sample, using the data provided. Also calculate the natural log of your K value.

K =

lnK =

3. Using the equation for the line that best fits the data or by carefully reading data from the graph, determine what temperature (in degrees C) corresponds to the value for the lnK you just determined. Show your work either by providing the equation and calculation or by drawing on the graph and showing your calculation.

4. The equation below can be used to calculate temperature, and was determined from the experimental work of Ferry & Spear (1978). It involves various thermodynamic parameters for garnet and biotite (enthalpy, enthalpy, volume), and is derived from the expression
$DG = DH - TDS + DVP + 3RTlnK_D$

$$T = (52112 + 0.238*P)/(19.51-24.942*ln(K))$$

*P in this equation is in **bars** and the T that you calculate is in **Kelvin**.*

Note that to calculate a metamorphic temperature, you need to have an estimate of pressure (similarly, to calculate a metamorphic pressure, you need to have an estimate of temperature). This may seem circular, since at the outset we don't know either P or T, but the situation is not hopeless.

• For thermometry, we use assemblages whose relative compositions do not vary much with pressure, so it doesn't matter what pressure you guess, as long as it's within the realm of geologically reasonable pressures.

Test this assumption by calculating temperature for your K value at 5 and 15 kbar.

T @ 5 kbar:
T @ 15 kbar:
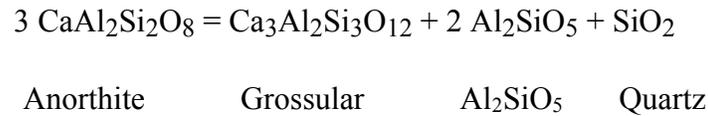
Is the garnet-biotite thermometer pressure-sensitive?

5. Now calculate temperatures for Samples X and Y using the mineral composition data to compute K, and the equation above to calculate T.

T of Sample X:
T of Sample Y:

Geobarometry: garnet-Al₂SiO₅-plagioclase-quartz

The equilibrium mineral assemblage garnet + plagioclase + quartz + Al_2SiO_5 (kyanite, sillimanite, or andalusite) can be described by the following pressure-sensitive reaction, written for the Ca end-members of garnet and plagioclase:

$$3\ CaAl_2Si_2O_8 = Ca_3Al_2Si_3O_{12} + 2\ Al_2SiO_5 + SiO_2$$

Anorthite   Grossular Al_2SiO_5 Quartz

An expression relating the compositions of the minerals to pressure is:

$$\Delta G = 0 = \Delta H - TDS + (P - 1)\ \Delta V + RT\ln K_{eq}$$

where $K_{eq} = \dfrac{X_{SiO_2}^{qtz} \cdot \left(X_{Al_2SiO_5}^{kyanite}\right)^2 \cdot X_{grossular}^{garnet}}{\left(X^{plagioclase}\right)^3}$

ΔH = -48,357 J/mole
ΔS = -150.66 J/mol-K
ΔV = -6.608 J/bar
(Ghent, 1976)

1. Using the data in the accompanying table, calculate the various mole fractions required in the expression above. Show your work.

2. Calculate the metamorphic pressure recorded by Sample X using this barometer and the temperature you calculated with the garnet-biotite thermometer. Express your answer in kilobars.

   P of Sample X:

3. Now redo the calculation for Sample Y.

   P of Sample Y:

4. How different are the results of your two calculations? Compare the temperature-sensitivity of this geobarometer to the pressure-sensitivity of the garnet-biotite geothermometer.

This program runs on a PC with DOS. Type TWQ to start the program.

- **UNIT ASSIGNMENT:** give location of the files, or accept all default files by hitting **ESC.**

- **SELECTION OF DIAGRAM VARIABLES;** the default is P-T and should be in bold characters when this window opens. Press **ESC** again to accept this option, or use arrow keys to move to the desired option, then press ESC.

- **GLOBAL OPTIONS:** enter the elements that you want the program to consider. ***** don't forget oxygen ***** and hydrogen if any minerals are hydrous or if you want water to be considered as a mineral. Use abbreviations from the periodic table, separated by spaces. End with a **<RET>**   **(CR = carriage return)**

    Pressure minimum/maximum in BARS. You must use a decimal point when entering a
new   pressure; press **<RET>** after entering a new pressure and the cursor will automatically move to the next value. If accepting defaults, just hit   **<RET>**.

    Temperature minimum/maximum in degrees C. Temperatures of metamorphic interest range from about 300-1000° C. Don't forget the decimal point if entering new T ranges.

    Fluid composition (mole fraction H_2O-CO_2): **choose $H_2O = 1$** if water or a hydrous
phase   is present.

    H_2O routine: options will be presented if H_2O is present; select default
    Use arrow keys to move down through lists.

    Plot output; select **STABLE CURVES** for assignments in this class.
    Label options; select **ABBREVIATIONS** (of mineral names)

Press **ESC** when done with this page of options.

Now you have a choice of minerals. Most likely, you will not want the program to consider every mineral that it lists.

- **PHASE SELECTION:** you will be given a list of every mineral in the database that contains some or all or the elements you selected. If you want to select a mineral, hit <RET> when the mineral name has the cursor blinking on its first letter. Use arrow keys to move through the list. If the list continues on another page, use the Page Down key. If you make a mistake and select a mineral you didn't mean to select, press the minus (-) key and the mineral will be de-selected.

NOTE: after you hit **<RET>** to select a mineral, you will be prompted for the *activity*. The default is 1. Hit **<RET>** again to continue (accept the default unless instructed otherwise).
When you are done, press **ESC**. You may quit at any time and start over by pressing **ctrl-Q**.

- **SELECTION OF SOLUTION MODELS:** If you have set up a file (e.g., rock.cmp) of mineral compositions, you can select solution models. The program will tell you which minerals it has models for. Use the defaults for this exercise. Follow the instructions at the top of the window for choosing models. When you are done, or if you don't want to do this, type **ESC**.

The program then goes to work and calculates all possible reactions and shows you its progress.

The output file will be stored in a file called PLOT.DAT. I recommend changing the name of this file right away so you don't overwrite it. To do this, exit the program (ESC), and type REN PLOT.DAT WHATEVER.DAT.

You can look at your diagram by running the program PLOT. If you have changed the name of PLOT.DAT, you will need to type PLOT *yourfilename* (if you don't include a filename, the default is PLOT.DAT). Type ESC to exit.

If you have constructed a simple diagram, it might be readable the way it is. If there are a lot of reactions, however, the labels can overlap and be difficult to read. If this is the case, exit the plotting program (ESC), and run a program called **CLEAN**.

- type CLEAN filename.dat (or you can type CLEAN and the program will prompt you)

- in the first window, you can input the filename, the output plot name, the output list of reactions, and the label size (0.25 is the default; you can adjust this if you want)

- type ESC to continue

- GLOBAL OPTIONS: you can select whatever option you wish; the default works just fine in most cases; type <RET> to continue

- the program kicks you out when it is done

Run PLOT again, but this time use CLEAN.DAT (or whatever you named your new output file).

Print the diagram when it is perfect (if you have graphics software for PC files you can fix the graphs by other means). Otherwise, you need to scan the awful-looking output and make it look nice using Adobe Illustrator or similar graphics program.