

Introduction to thermodynamic modeling software

In this exercise we will be using the thermodynamic modeling software, written by Christian de Capitani, University of Basel, Switzerland:

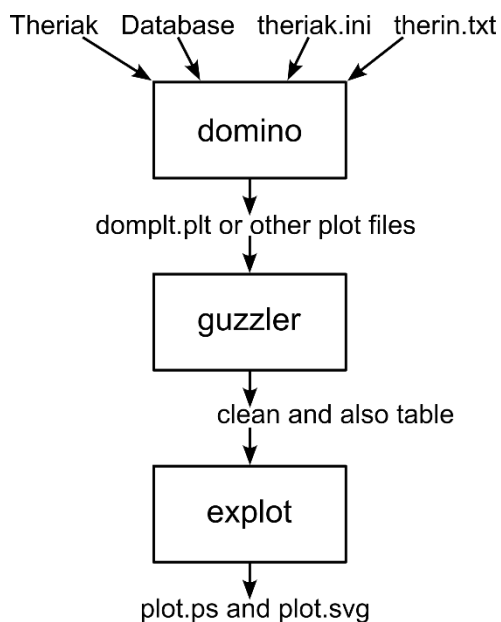
<https://titan.minpet.unibas.ch/minpet/theriak/theruser.html>

The purpose of this exercise is to introduce you to the realm of sophisticated modeling software in general (also available in the fields of groundwater flow, water chemistry, geophysics, and essentially every other geosciences field), and to better introduce you to the nature of metamorphic chemical reactions. The implementation of Theriak-Domino we will use was made by Douglas Tinkham, Laurentian University, Ontario:

<https://dtinkham.net/peq.html>

This version is easy to install on Windows computers, but is otherwise essentially the same as de Capitani's version.

Theriak-Domino, like most other implementations of thermodynamic software, is run from a command line interface. That means no graphical interface with buttons and menus. Maintenance of the thermodynamic software itself is hard enough, without adding on maintenance of a graphical user interface, too. Though the command line interface may be unfamiliar, it is relatively easy to use, and log files let the software remember past inputs, so in many cases you can just press ENTER and don't have to type anything in. Here is the general software use sequence:



This is what the different programs do (partially copied from the University of Basel link, above).

Theriak: The heart of the collection, calculates the stable mineral assemblage and phase compositions for a given rock (bulk composition) at specified P-T conditions.

Domino: May calculate (a) equilibrium assemblage diagrams with selectable axes (P, T, component activity, logarithm of component activity), (b) Pseudo-binary or pseudo-ternary phase diagrams, (c) Phase compositional isopleths as well as density, volume, or modal amount distributions; (d) Distribution of rock bulk parameters. Basically, Theriak does the calculations, and Domino uses Theriak many times across a P-T-X-activity adaptive grid to make a diagram (phase diagram, graph, whatever).

Guzzler: Takes the output of Domino, and extracts from it the reaction lines and other information, and decides where to put labels.

Explot: Takes guzzler output and transforms that into 'ready to use' postscript (.ps, readable by Adobe Acrobat etc.) and Scalable Vector Graphics (.svg, Inkscape, etc.) files that can be viewed on screen or printed.

Therbin, Therter, Thalia, and Thermo are other programs in the package that calculate other types of diagrams. We won't be using those.

The database file contains the thermodynamic constants for all phases the software will consider. Different databases have somewhat different sets of phases, which may have somewhat different thermodynamic constants to help make the database "internally consistent." The database we will use is especially for metamorphosed shales, and so is not suitable for metamorphosed basalts, limestones, or ultramafic rocks. Theriak.ini is a text file containing default file names and other information that the different programs need. We won't be touching that file.

The file we will be manipulating is called therin.txt. The only thing we will be worried about there is the chemical composition given to domino (and thus to theriak). This line is down at the bottom, and may look something like this:

```
1  NA(0.5)MG(0)AL(3)SI(10)K(0.5)CA(0)TI(0)MN(0)FE(0)H(10)O(?)O(0.00)  *
```

The format has to stay like this. The 1 at the beginning is for screen output. Leave it at 1. The next part has the chemical composition to be used in the calculation. The software only considers one composition at a time. The values must be in molar proportions, and so can be easily calculated by listing the minerals you are interested in to define the composition, and summing the quantities of each element in their formulae. The * at the end says to use all pertinent phases in the database. Comments can follow this.

To have saturated, or always present phases, just add in a lot of the elements needed to make those phases. In this example, the system will always be saturated with quartz and H₂O fluid, so lots of Si and H have been added. O(?) near the line end tells the program to give stoichiometric amounts of oxygen to each of the elements to the left (FeO, SiO₂, etc.). O(0.00) at the very end lets you add excess oxygen to make Fe³⁺ (Fe₂O₃). For example, if you have Fe(10), it will start out as all FeO. However, if you then have at the end O(1), one oxygen will be added to the FeO to make 8 FeO and 1 Fe₂O₃.

The Al-silicate polymorphs, P-T

1. Set up a spreadsheet with Al-silicate, quartz, and H₂O labels in a column. In a row above, put the elements present (Al, Si, H, but not oxygen, because the software will use O(?) to calculate that for you).
2. In this phase-element table, put in the stoichiometric (formula, molar) amount of each element in each phase. You will want this system to be H₂O- and quartz-saturated, so multiply the amount of quartz and H₂O by some reasonable factor (e.g., 5), so they will always be in excess. Basically, you need enough so that even the most hydrous and silica-rich Al-silicates will still leave excess quartz and H₂O.

	Al	Si	H
Al-silicate	2	1	0
Quartz x 5	0	5	0
H₂O x 5	0	0	10
Total	2	6	10

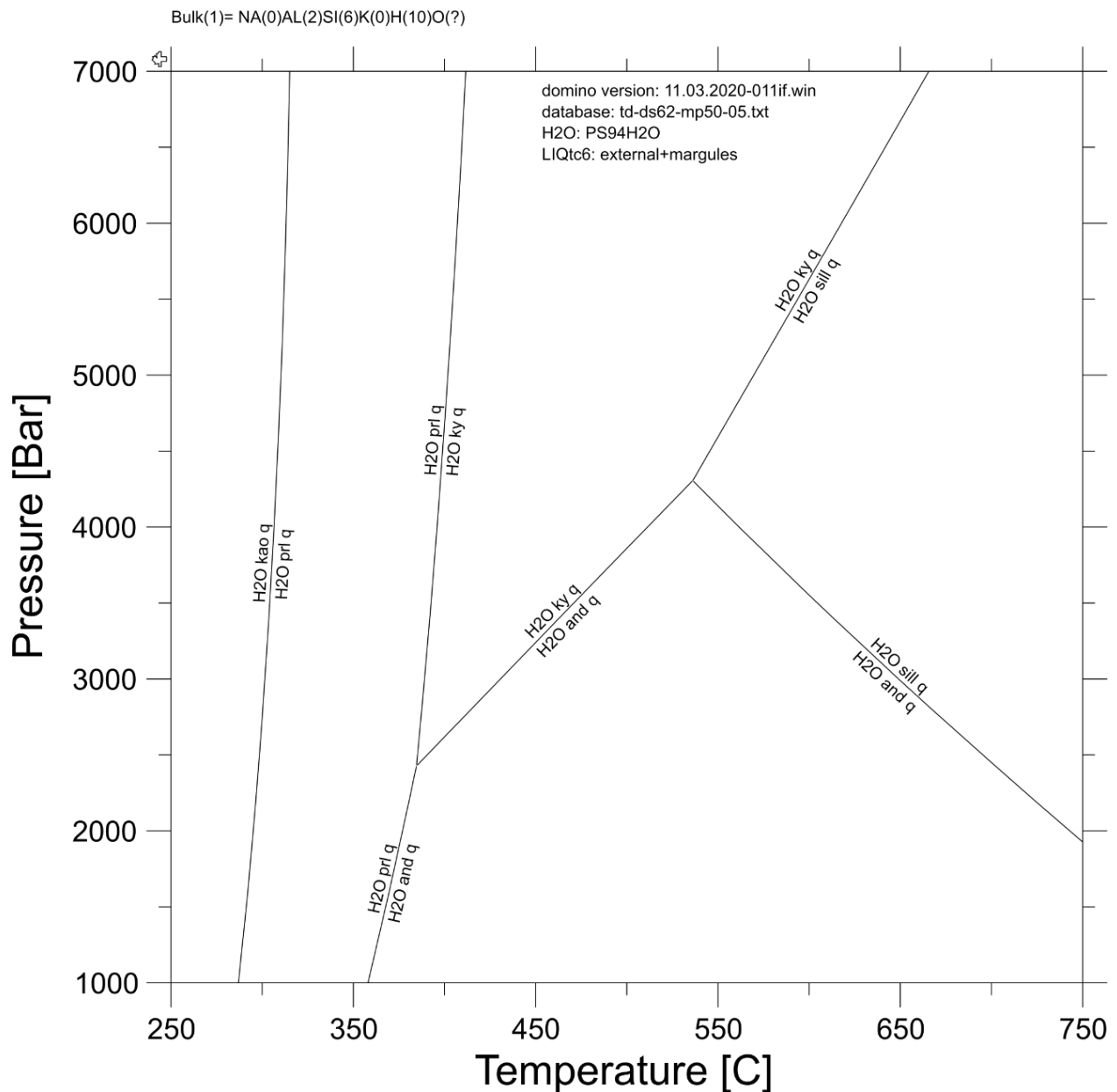
3. Calculate the total of each element.
4. In the Working folder, open the **therin.txt** file. Change the element amounts in the bottom line to the values you have, or zero otherwise. **Save the file**. The bottom line of the file should look something like this:

1 NA(0)AL(2)SI(6)K(0)H(10)O(?) *

5. In the Working folder, double click on **start.bat**. A black window will open, giving you a C: prompt.
6. At the first prompt, type: “**domino**”, then press Enter.
7. **Database definition:** Type “**td-ds62-mp50-05.txt**”, unless this is already the default.
8. We’ll be doing a P-T phase diagram.
9. **Definition of X-axis:** Type “**TC 250 750**”. Values are in degrees Celsius. Note that you must have *at least* two spaces between each part.
10. **Definition of Y-axis:** Type “**P 1000 7000**”. Values are in bars. Again, you must have at least two spaces between each part.
11. **Definition of calculation type:** Type “.” for an equilibrium phase diagram.
12. **Labeling reactions...:** Type “1”. This labels each reaction line with all phases present on each side of the line (unless there is no room, then see the **table** file for numbered lines).
13. Domino will finish its calculations, returning you to the C: prompt.
14. Type in “**guzzler**” and press **Enter**. Guzzler takes in all the information produced by Domino, and extracts just the reaction line information.
15. **Enter...graphics file name:** Type “**domplt.plt**”. This is the plot file that domino put all its information in.
16. **Enter...X...width:** Press **Enter** to accept the defaults from domino.

17. **Enter...Y...height**: Press **Enter** to accept the defaults from domino.
18. **Enter ...size of labels**: Accept the default of **0.2**.
19. **Enter ...option (min_length)**: Accept the default of **0.020**.
20. Guzzler will finish its calculations, returning you to the C: prompt.
21. Type in “**explot**”, and press **Enter**.
22. **Enter...graphics file name**: Type “**clean**”, the file where guzzler puts its results.
23. Explot will finish its calculations, returning you to the C: prompt..

You should see three new files in the Working directory. **Table** is a text file of numbered reactions, produced by Guzzler that are present in the phase diagram. Open it with Notepad or other text editor. **Plot.ps** and **plot.svg** are two graphics files that contain your phase diagram. **.ps** stands for postscript, which can be read by Acrobat or other programs. **.svg** stands for Scalable Vector Graphics, and can be read by Inkscape, many web browsers, and other programs. Open the **.ps** file with Acrobat. It should look more or less like this:



The line labels are assemblages (not balanced reactions) on either side of the reactions. Notice that all have H₂O fluid and quartz, making clear that both phases are present (saturated) in all assemblages. Make sure you know what all the abbreviations mean. Save this as a .pdf file in a new folder, and also add **.txt** to the table file name and save it in the same folder, along with the **therin.txt** and **.svg** files. It is best to also change the file names (not the extensions) so that you know what's in each file (e.g., **Alsilicate-Qtz-H2O.txt**).

What do the labels in the reactions mean?

Reactions are normally labeled with the phases that participate in the reactions, or their obvious abbreviations (e.g., **Musc + Qtz = Ksp + H₂O**). One of the problems with thermodynamic software is that each phase is actually represented by a model: a mathematical

construct that includes constants for enthalpy, entropy, volume, heat capacity, and so on, and for solid solutions also the energies of end member mixing. Dozens of these have been developed based on natural, experimental, and/or theoretical work, and each one has to be distinguished from other possible models in the thermodynamic database. In this last model, **prl** is the model for pyrolocite, as defined in the database, and H₂O is the model for that fluid.

Prl is a comparatively simple model, not involving any solid solutions. You will soon see others like FSP4TR, for K-Na-Ca ternary feldspar solid solutions, LIQt6 for silicate liquid solutions, and WM for white mica (paragonite-muscovite) solid solutions. To see what each model is, and what it consists of, open the **td-ds62-mp50-05.txt** file and search for the model name (FSP4TR, WM, and so on). Just don't change anything in that file. If you do, it's likely not to work correctly.

What to turn in for this exercise:

The phase diagram.

Micas and feldspars in pelitic schists, P-T

Here we're going to look at the micas, feldspars, and Al-silicates with metamorphic grade. Start by making another table, like the one in the first exercise. However, this time make the table with one muscovite, one paragonite, and sufficient quartz and H₂O to always keep the system saturated in those phases. How do you know if it is always saturated in those? Look at the **table** output assemblages. If quartz and H₂O are not part of every assemblage, add some more of what is missing to the last line on your **therin.txt** file.

Phase	Al	Na	K	Si	H
Quartz	0	0	0	5	0
H ₂ O	0	0	0	0	10
Muscovite	3	0	1	3	2
Paragonite	3	1	0	3	2
Total	6	1	1	11	14

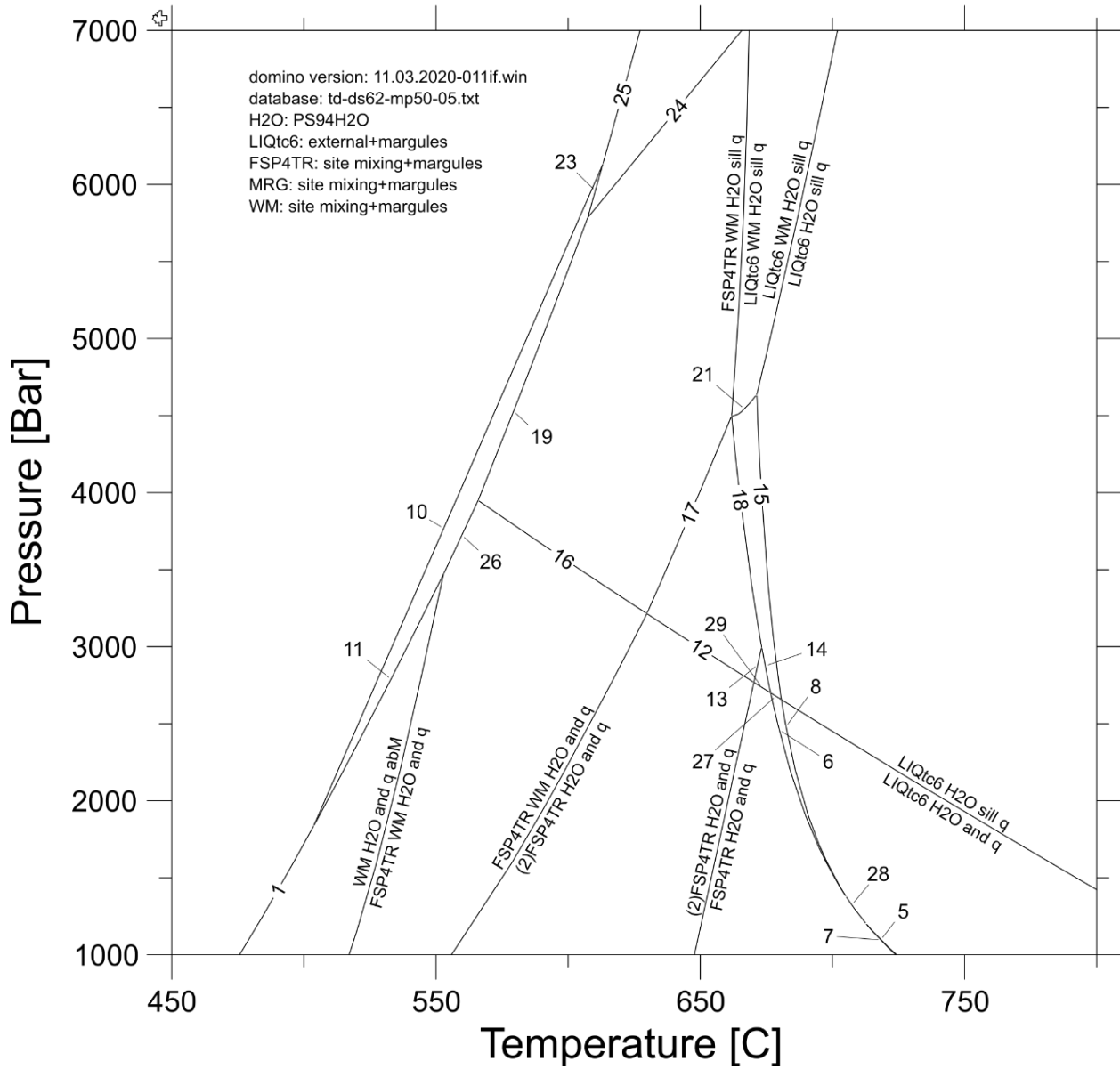
The bottom line of your **therin.txt** file should look something like this:

```
1  NA(1)AL(6)SI(11)K(1)H(14)O(?) *
```

Run **domino**, **guzzler**, and **explot** the same as before, except in **domino** change the temperature range to 450 to 800°C (**tc 450 800**).

Check that the resulting graph (from **explot**) has H₂O and quartz in all assemblages. If not, add more of what you need and re-run. When the results show all assemblages having excess quartz and H₂O fluid, save the **therin**, **plot**, and **table** files in a new folder, as before. The result should look something like this:

Bulk(1)= NA(0.5)MG(0)AL(3)SI(10)K(0.5)CA(0)TI(0)MN(0)FE(0)H(10)O(?)O(0.00)



What to turn in for this exercise:

Label all of the fields with their assemblages, omitting quartz and H₂O fluid, which are everywhere (note that 8 fields are already labeled, the rest you can figure out using numbered assemblages on either side of reactions lines in the table.txt file). Also, highlight in some easily recognizable way these three different fields: the area where white micas are stable, the area where silicate liquids are stable (the low temperature limit of this area is the solidus), and the line within which there are two feldspars. Most of the divariant fields aren't labeled because of lack of room). You can do the labeling by hand or using an .svg editor like Inkscape.

Micas and feldspars in pelitic schists, isopleths

This time we'll extract composition information from the results.

1. Run **domino** again, with the same **therin.txt** file as the last exercise. The database file, T range, and P range will also be the same.
2. When you get to the **definition of calculation type**, type "i", for isolines.
3. Type in "1" for isopleth (iso-composition lines). You have lots of other options, too.
4. Type in "2" for **FSP4TR**, the ternary feldspar solution model.
5. Type in "4" for isopleths of **K in the A-site of the feldspar**.
6. You can obviously have sodium and potassium-rich feldspars coexisting, so you have to say which phase (ab or san = 1 or 2) is the one to pay attention to. You can only get isopleths of one phase at a time. (Na(A), K(A), Al(T), and Si(T) aren't phases, they are crystallographic site occupancies. Where it asks for **Sorting order for FSP4TR**, pick "2" for san.
7. For isopleth range and spacing, give "**0 1 0.05**". Remember two or more spaces.
8. **Labeling of reactions, precision and smoothness**, type "1".
9. When **domino** finishes, Run **guzzler** and **explot** as before. Change the plot file names as to reflect K-feldspar and K content isopleths, and put these in their own folder. Compare to the reaction diagram. You will see that the K-rich feldspar (of two feldspars) occurs only in the two-feldspar field. The isopleth diagram should look like the graph below.
10. Repeat what you did starting at 1 again, but this time at **Sorting order for FSP4TR**, pick "1" for ab.
11. Again, for the isopleths, give "**0 1 0.05**".
12. **Labeling of reactions, precision and smoothness**, type "1" as usual.
13. This will take a little longer to run.
14. Run **guzzler** and **explot** as before.
15. Change the plot file names to reflect albite and K-content isopleths, and put these into the same folder as the K-feldspar files.
16. Here on the plot you see that the Na-rich feldspar can be found in all areas where there are feldspars, including the smaller area where there are two feldspars.

So, what's happening? It turns out that paragonite dissolves into muscovite, increasingly at high temperature, but paragonite starts to dehydrate at higher temperature to make Na-rich feldspar (actually, to the lower-left you can see an albite (abM) bearing field, where the pure end member is calculated to be more stable than the solution model FSP4TR.

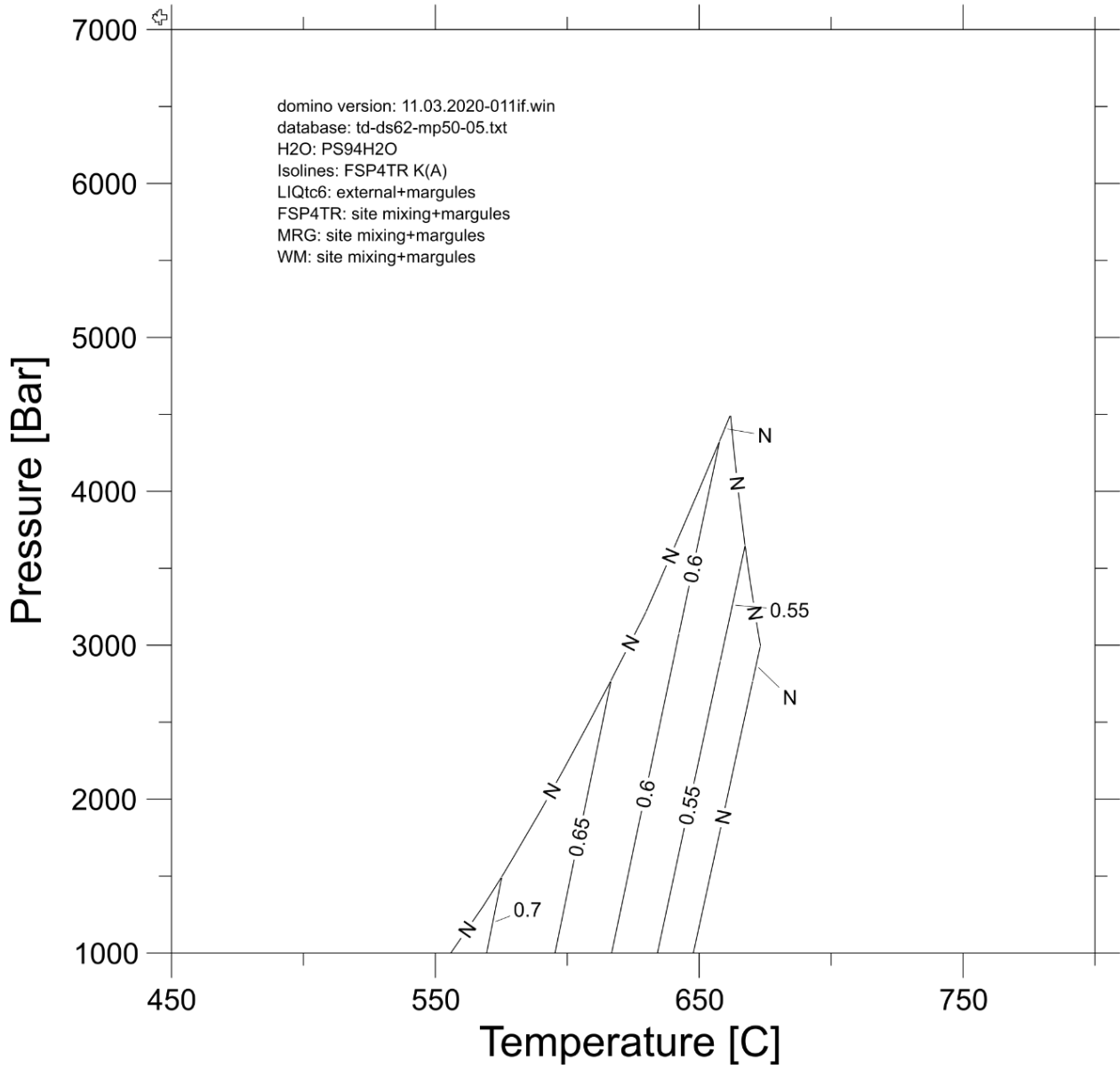
Muscovite progressively dehydrates, too, becoming increasingly K-rich, producing a separate K-feldspar phase in the lower-middle of the P-T field. At 650°C and a little higher, the top of the alkali feldspar solvus is reached, and so we have only one intermediate feldspar at those temperatures (possibly to become mesoperthite during cooling).

Do another one, showing H₂O content isopleths in the liquid solution model, LIQtc6. Note that, for the **Sorting order for LIQtc6**, you can't pick H₂O if that's what you want the isopleths for.

What to turn in for this exercise:

Hand in the three isopleth graphs. On the H₂O in LIQtc6 graph, show where the solidus is supposed to be.

Bulk(1)= NA(0.5)MG(0)AL(3)SI(10)K(0.5)CA(0)TI(0)MN(0)FE(0)H(10)O(?)O(0.00)



Micas and feldspars in pelitic schists, ternaries

Change your **therin.txt** file bottom rows to this:

```
1    NA(0)AL(2)SI(10)K(0)H(10)O(?)    *
1    NA(0)AL(1)SI(10)K(1)H(10)O(?)    *
1    NA(1)AL(1)SI(10)K(0)H(10)O(?)    *
1    NA(0)AL(2)SI(10)K(0)H(10)O(?)    *
```

Row 1 is sillimanite

Row 2 is K-feldspar

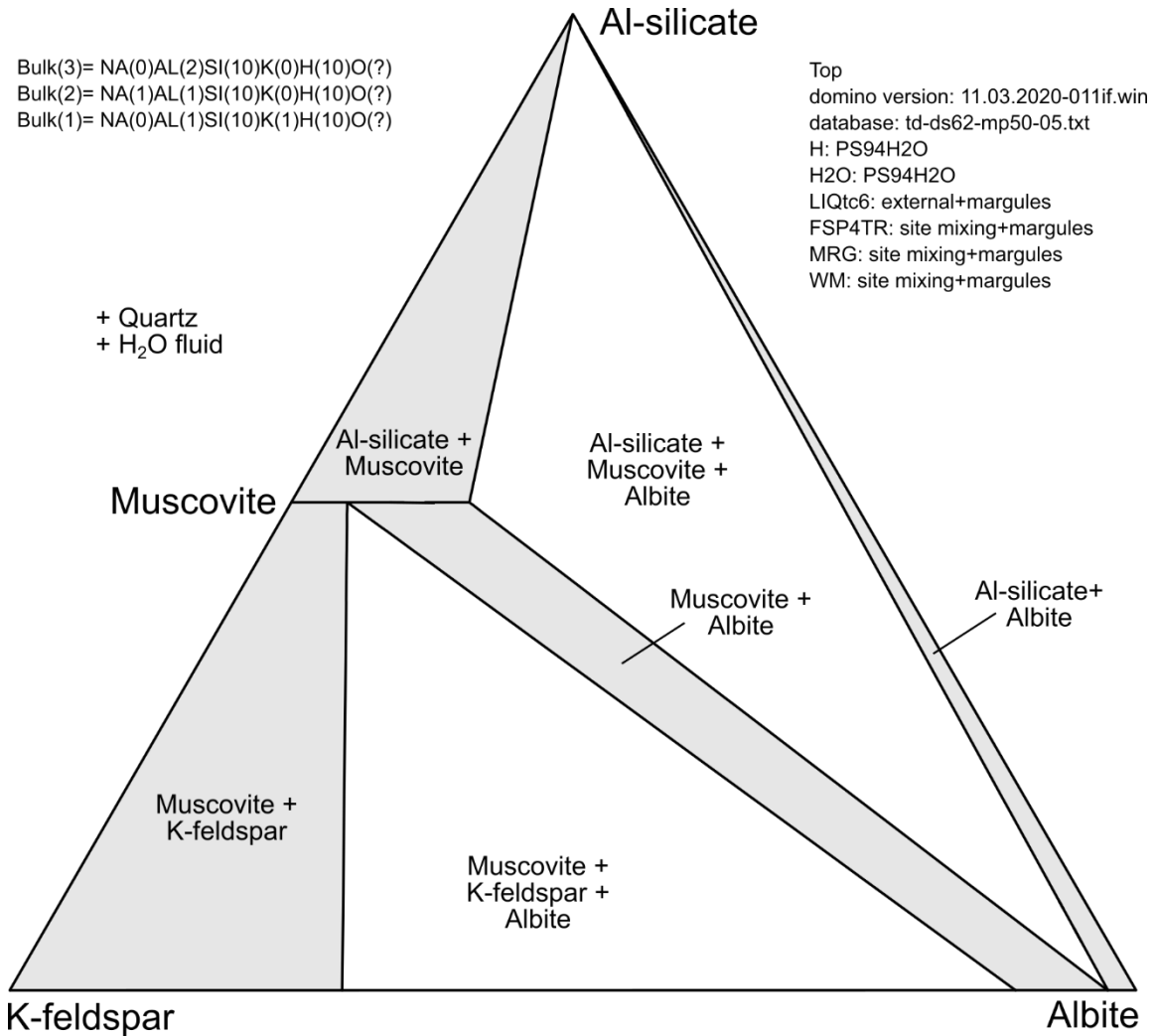
Row 3 is albite

Row 4 is a repeat of row 1 (I don't know why it needs this, but it does).

These represent corners of a ternary phase diagram, and all have excess quartz and H₂O so sheet silicates can be made. Save the **therin.txt** file.

1. Run Domino, using this new **therin.txt** file. The database file will be the same.
2. **Definition of X-axis:** Type “**TER**”, for ternary.
3. **Enter Temperature in deg. C:** Type “**625**”, without any tc.
4. **Enter Pressure in Bar:** Type “**6000**”, without the p.
5. **Definition of calculation type:** Type “.” (equilibrium assemblage).
6. **Labels:** Type “**1**”, for assemblages.
7. Domino calculations are done.
8. Run **guzzler**.
9. **Enter... graphics file name:** Type “**domplt.plt**”, the domino output (plot) file.
10. **Enter...width:** Accept defaults by pressing **Enter**.
11. **Enter...height:** Accept defaults by pressing **Enter**.
12. **Enter...size of labels:** Accept default by pressing **Enter**.
13. **Enter...min_length:** Accept default by pressing **Enter**.
14. Guzzler calculations are done.
15. Run **explot**.
16. **Enter...graphics file name:** Type “**clean**”, the guzzler output file.
17. Explot calculations are done.

The result of this calculation set should be a ternary phase diagram, labeled with the phases on either side of lines. There is the diagram, after being cleaned-up and edited (svg file in Inkscape), so that it's easier to interpret:



The gray areas are 2-phase tie-line fields, the white areas are 3-phase continuous reaction fields. The lower edge of the bottom white area is the alkali feldspar solvus. You can see that K-feldspar dissolves a lot more albite than albite does K-feldspar. The solution phases that were considered included LIQt6 (silicate liquid, version 6), FSP4TR (ternary feldspar, version 4), MRG (white mica solution model that works better with calcium micas), and WM (white mica that is the default mica solution model).

What to turn in for this exercise:

Just the phase diagram, with all 2- and 3-phase fields labeled with their assemblages (excluding quartz and H₂O fluid, which are everywhere).

Isobaric section showing phase relations, 4000 bars

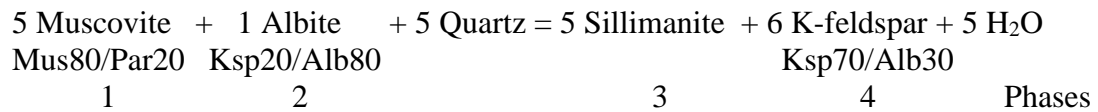
Use the same **therin.txt** file to make 6 ternary diagrams like above, except make all at 4000 bars, and temperatures of 525, 563, 610, 657, 669, and 690°C. See how 3-phase continuous reactions move. Collisions and separations of 3-phase fields from intermediate 4-phase fields correspond to the reaction lines in the previous P-T diagram you made.

What to turn in for this exercise:

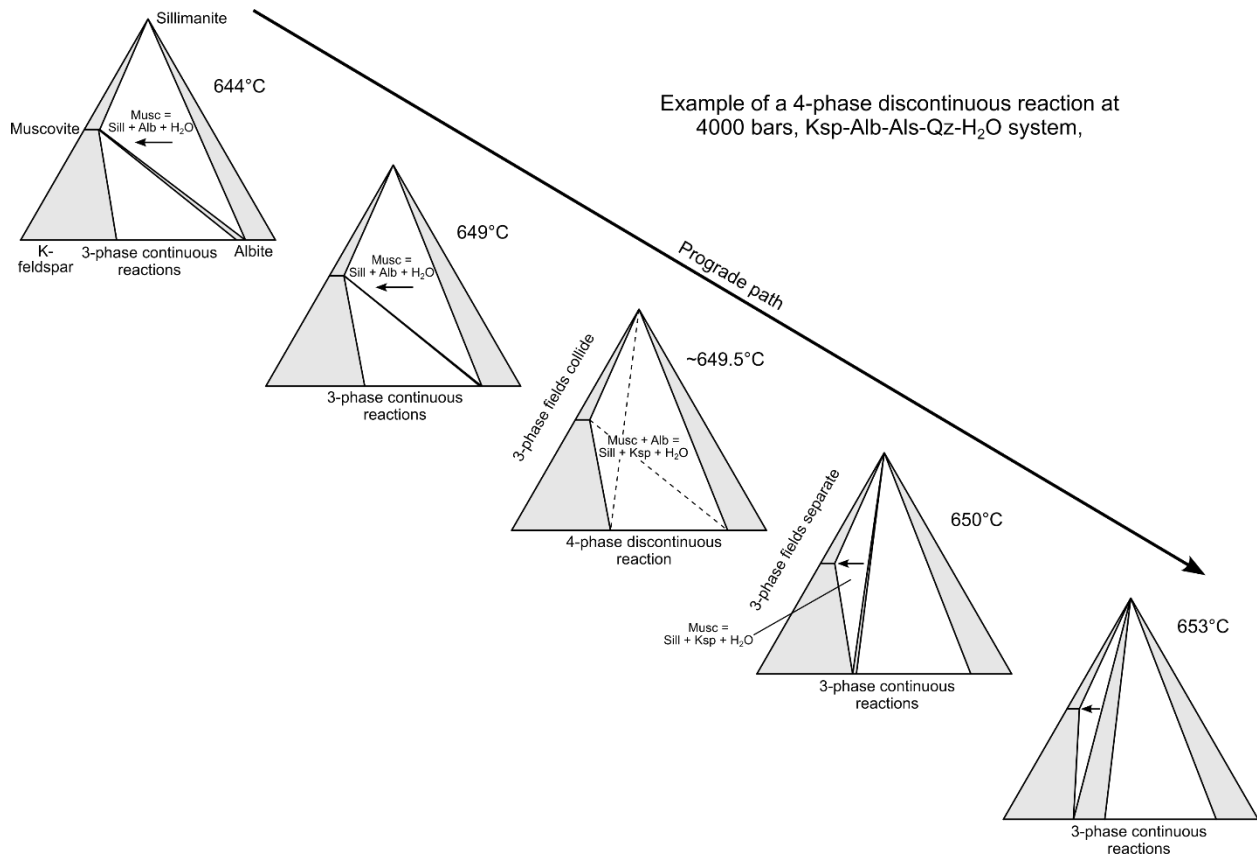
The six phase diagrams.

Isobaric visualization of a 4-phase, discontinuous reaction

Use the same **therin.txt** file to make 4 ternary diagrams like above, except make all at 4000 bars, and temperatures of 644, 649, 650, 653°C. Put them in sequence to see the 4-phase, discontinuous reaction (balance is approximate):



The sequence of phase diagrams should look something like this, but here the extra, middle one at ~649.5°C is a cartoon that can't be reproduced in Theriak-Domino. Note that the triangles, with K-feldspar and albite along the base, don't move much.



What to turn in for this exercise:

The four phase diagrams.

P-T for a more realistic schist, extracurricular

Use a spreadsheet to put in the assemblage biotite-muscovite-chlorite-quartz-H₂O fluid. For biotite, take the Mg/(Mg+Fe) ratio to be 0.4, and for chlorite to be 0.5. Chlorite is usually a little more Mg-rich than coexisting biotite. Use temperatures of 450-800°C, and pressures of 1000-7000 bars, like the micas and feldspars phase diagram. This run will take a while, because there are many more phases and extra (Fe-Mg-Al-Si) solid solutions to worry about. The calculation time increases more or less exponentially with the number of things that have to be worried about. With excess quartz and H₂O fluid, your

	Mg	Al	Si	K	Fe	H
Biotite	1.2	1	3	1	1.8	2
Muscovite	0	3	3	1	0	2
Chlorite	2.25	3	2.5	0	2.25	8
Quartz	0	0	~20	0	0	0
H₂O	0	0	0	0	0	~20
Sum	3.45	7	~30	2	4.05	~30

Because you have added iron, and because there is a Theriak program instability if the system has Fe²⁺ but no Fe³⁺, the last line of your therin.txt file should look something like this, with a little bit of extra oxygen added at the end.

1 NA(0)MG(3.7)AL(6)SI(25)K(2)CA(0)TI(0)MN(0)FE(4.3)H(22)O(?)O(0.01) *

For an even more realistic schist, do the same thing but add 0.5 paragonite. That will take even longer. How long can these runs take? The two shown here at the end might take an hour. I've had runs that involve amphiboles, with a lot of solid solutions to worry about, that took over 8 hours. Better than doing it by hand, though.

Theriak-Domino, and the other similar thermodynamic software packages, can do a lot more than you see here. This is enough for now, though.