

A tutorial for geochemical modeling of fluid-rock interaction using GEM-Selektor and the MINES thermodynamic database

Alexander Gysi

2020-12-02

Contents

Prerequisites	5
1 Create your first project in GEMS	7
1.1 Installing the MINES thermodynamic database	7
1.2 Creating a new project from scratch	8
1.3 Your first fluid-rock equilibrium model	11
1.4 Outcomes	12
2 Feldspar reaction path	17
2.1 Compute the chemical equilibrium of single chemical systems (SysEq)	17
2.2 Compute a titration model (Process, S mode)	19
2.3 Modify P-T of the feldspar reaction path	23
2.4 Tweak and plot the results	25
2.5 Compute a cooling model (Process, P mode)	26
2.6 Outcomes	31
3 Module 3	35
4 Module 4	37
5 Module 5	39

Prerequisites

GEM-Selektor (GEMS), is a numerical modeling program with a graphical user interface based on Gibbs energy minimization and permits calculating and solving fluid-rock interaction problems of interest in geochemistry.

- Installation instructions for GEMS and more information about this modeling program can be found on the GEMS team webpage: <http://gems.web.psi.ch/GEMS3/techinfo.html>.
- Information about the MINES database and project files for the tutorials can be found under <https://geoinfo.nmt.edu/mines-tdb>

This booklet is subdivided into five modules.

- Module 1: Create your first project in GEMS and installing the MINES database

Chapter 1

Create your first project in GEMS

Here we will learn how to create a new Project, the selection of thermodynamic databases, components and equations of state for your modeling project. We will also explain the project folder structure and how to install the MINES thermodynamic database for modeling hydrothermal fluid-rock interaction and ore-forming processes . You will also learn how to interact basalt with water in your first equilibrium calculations.

1.1 Installing the MINES thermodynamic database

The MINES thermodynamic database can be downloaded at <https://geoinfo.nmt.edu/mines-tdb> (Fig. 1.1).

- Download and unzip the DB19.default archive folder to Downloads. Select all the database files in this folder and copy them (Fig. 1.2).
- Merge these database files with the Gems3-app/Resources/DB.default folder by pasting them into DB.default (Fig. 1.3).

In Linux this folder is in /Gems3-app/Resources/DB.default; In Mac OSX this folder is in /Applications/gems3 then right-click show package content and go to Contents/Resources/DB.default; In Windows this folder should be in /Gems3-app/Resources/DB.default.

The folder structure of the GEMS program, independent of the operating system used, consists of two main folders:

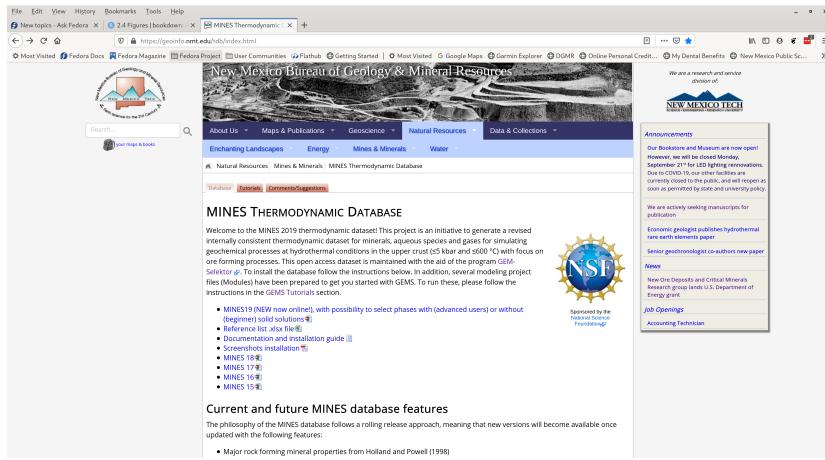


Figure 1.1: The MINES thermodynamic database webpage and files to download. Select the weblink for MINES19.

- Gems3-app
 - The GEMS3-app folder contains the program resources and also a subfolder Resources/ DB.default, which will be used to copy the MINES thermodynamic database files into it.
- Library/Gems3/projects
 - The projects folder will contain all the projects you create and work on, and will also be the folder in which you can copy the tutorial folders.

1.2 Creating a new project from scratch

- Open GEMS and click **New Project** in the Modeling Projects window. Give a name to your project (no spaces). The user interface is shown in Figure 1.4.
- In the next window, you can choose the thermodynamic database for your project. Select the database files 3rdparty/MINES and support, then deselect other databases as shown in Figure 1.2. Click **Next**.

*Do not forget, you have an extensive list of minerals included in this database. Once you have gone through the tutorials and are familiar with GEMS, it is suggested that in thermodynamic database mode you switch to the **Phase** module (Fig. 1.8), and remove minerals that are not relevant for your own specific*

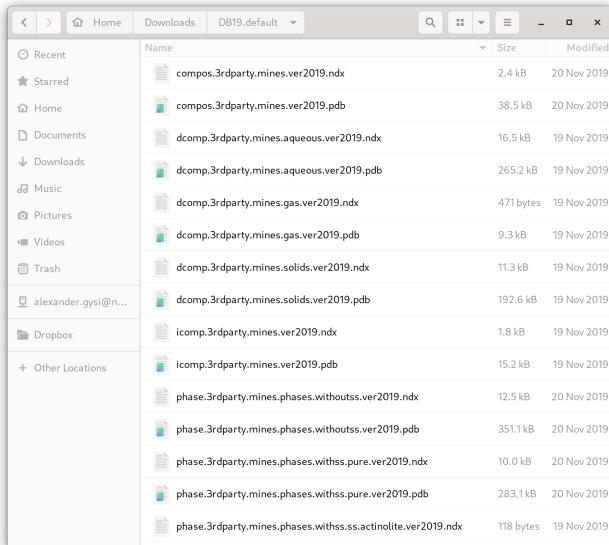


Figure 1.2: Unzipped DB19.default folder and database files to copy.

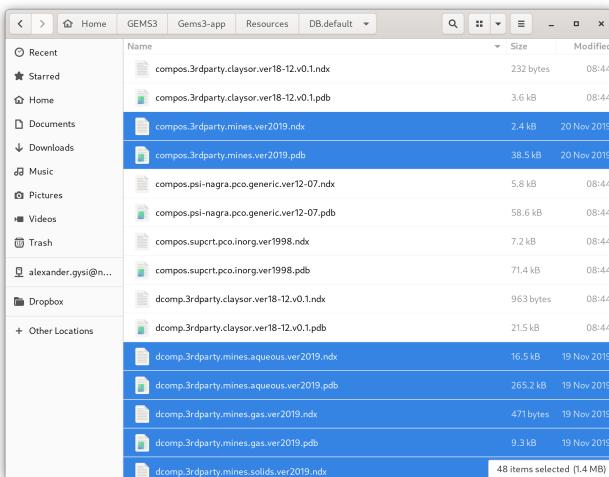


Figure 1.3: Database files merged with the Gems3-app/Resources/DB.default folder in GEMS.

project. Also, for less advanced users, it is easiest to not use the ternary non-ideal feldspar solid solution model (*ss*) but only their end members (i.e., anorthite, albite and microcline).

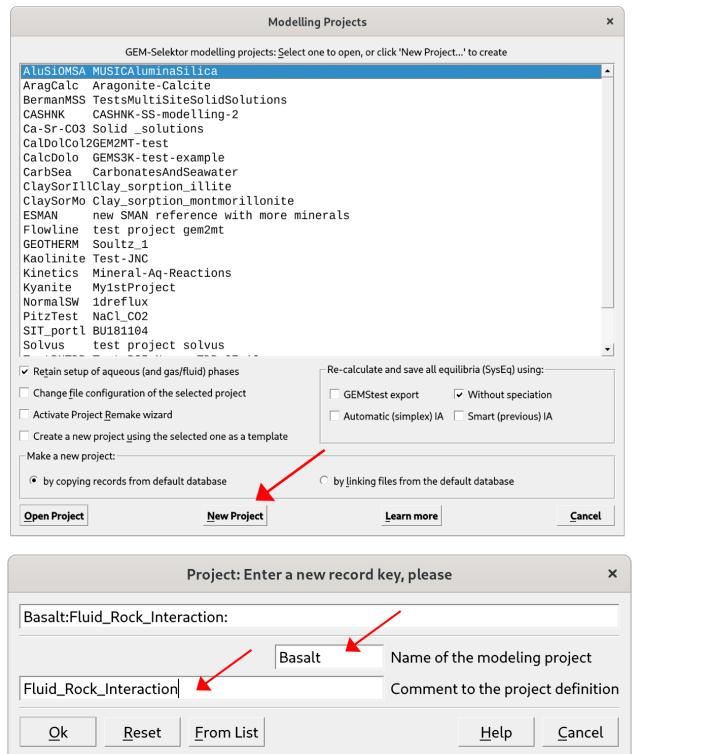
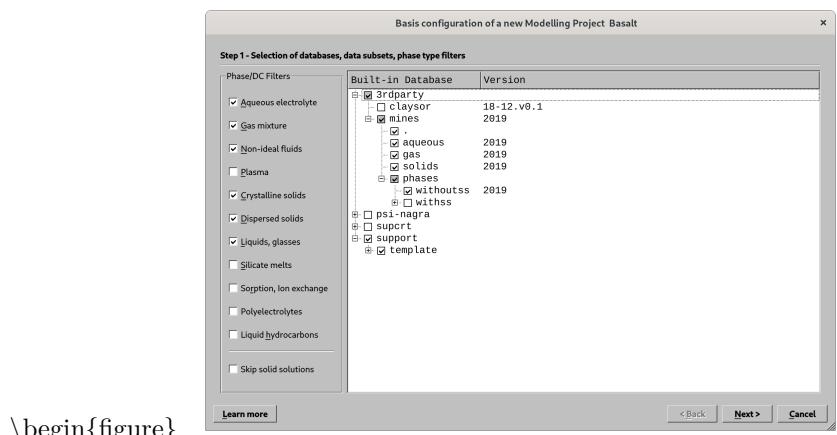


Figure 1.4: GEMS user interface showing the project window. Click on make a ‘New Project’ and select a project name without spaces.



\begin{figure} \cap-

tion\{Select 3rdparty/mines and support, and for phases select only withoutss.
Note that we recommend only advanced users to choose withss; the expanded tab shows pure for endmembers and ss for different solid solution endmembers\end{figure}

- In the next window choose your system components: H-O-C-Cl-Na-K-Ca-Mg-Al-Fe-Si-Ti (Fig. 1.5). Have you checked you got all of the elements selected? Check again please, then click **Next...** By doing so, GEMS will automatically look up all phases with these components in the MINES database and copy them into your modeling project! *Tip of the day: all your modeling projects you are working on are located under Library/Gems3/projects. Make sure to do regular backups...*
- In the next window you will be able to choose the activity model for your aqueous speciation calculations (e.g. “Debye-Hückel”, Davies equation, ...), and the EOS for gases. For now, follow Figure 1.6 using the extended “Debye-Hückel” equation (Helgeson), check the parameters and click **Check** for the aqueous speciation model. *This model is ideal for modeling H₂O-NaCl aqueous solutions (with NaCl as background electrolyte) at hydrothermal conditions at relatively moderate salinities observed in many ore deposits.*
- Then you can switch to the gas EOS model tab and choose the Peng-Robinson-Stryjek-Vera (PRSV) model and click **Check** (Fig. 1.6). That’s it, now you are ready to model your first equilibrium model!

Note: this model is for non-ideal gases, and for this purpose a new phase with the acronym (f) was added to the MINES database with all the relevant parameters using the PRSV EOS. Else the choice would be the ideal gas law with a phase using the acronym (g)

1.3 Your first fluid-rock equilibrium model

- In the next window, you will be able to define the name of your first fluid-rock system equilibrium (**SysEq**) calculations and set the pressure and temperature (Fig. 1.7).
- Add a name without spaces and P-T conditions, i.e. we choose basalt-fluid, 250 °C for T and 1 kbar for P.
- Next window we select our ingredients and add 1000 g of H₂O (Aqua), 200 g of NaCl, 5 g Gas CO₂ and 500 g of basalt (Fig. 1.7). Click **OK**.
- Finally, you can click on **Calculate BCC** followed by **Calculate equilibrium with GEM** as shown in (Fig. 1.8). You can easily create

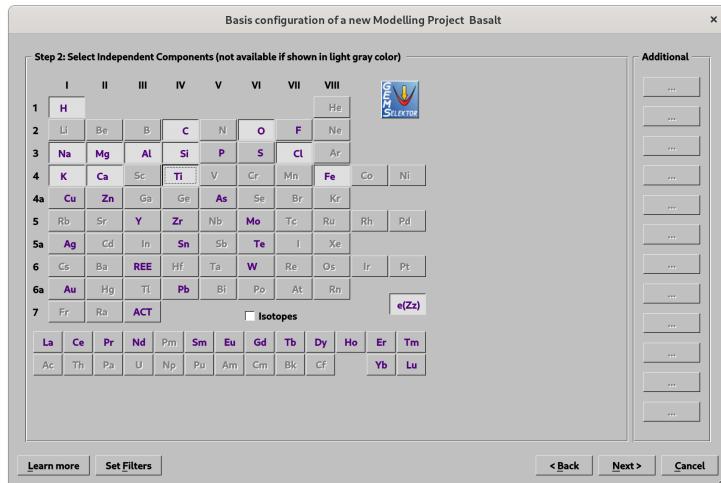


Figure 1.5: Select here the composition of the system. All phases containing these elements will automatically be loaded from the MINES database into your project.

another system by selecting **Clone a new record from this one** and change the fluid/rock ratio or temperature and see what happens with the results.

1.4 Outcomes

Congratulations! In Module 1 you learned how to install the MINES thermodynamic database in your Resources/DB.default GEMS folder, the general folder structure of GEMS, how to setup your first project and how to run your first fluid-rock equilibrium calculations in GEMS.



Figure 1.6: Select here the activity model for aqueous speciation (a-d) and the EOS model for gases (e-g).

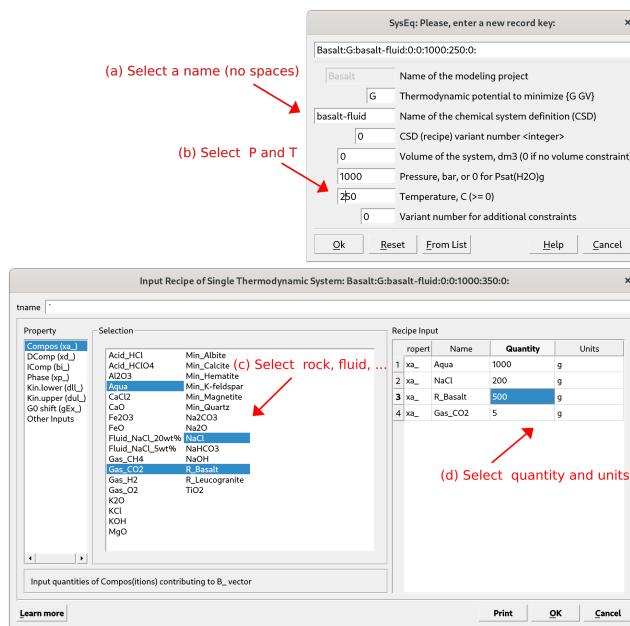


Figure 1.7: GEM-Selektor user interface showing the windows to create a new equilibrium system and define pressure (P) and temperature (T) for our first calculation.



Figure 1.8: GEM-Selektor user interface showing how to ‘Calculate BCC‘ followed by ‘Calculate equilibrium with GEMS‘. Also shown are the ‘Equilibrium Calculation‘ mode and the ‘Thermodynamic database‘ mode, where you can inspect the MINES database.

Chapter 2

Feldspar reaction path

In this tutorial, you will learn to model the reaction path of K-feldspar in contact with a NaCl-bearing aqueous solution and calculate the evolution of the fluid and the minerals formed as a function of increased fluid-rock interaction. You will also learn how to set up an automated cooling process simulation and plot results from multiple simulations. We will use the GEMS project file “Module2” that can be found either in the /Tutorial/Module2_fsp-reaction/unsolved workshop folder or download it directly [here](#).

2.1 Compute the chemical equilibrium of single chemical systems (SysEq)

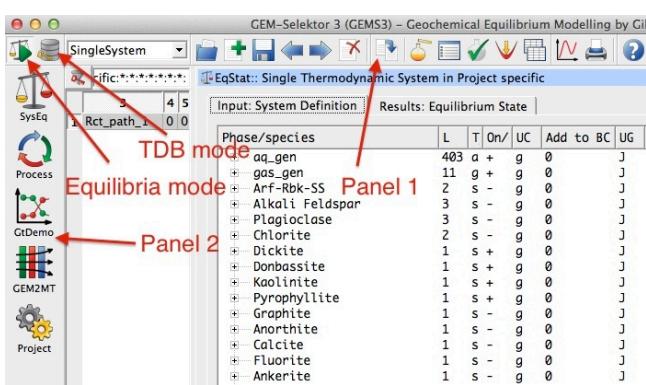


Figure 2.1: GEMS user interface showing the ‘Equilibria Calculation’ and ‘Thermodynamic Database’ modes.

- Copy the entire unzipped Module2 folder into your GEMS project directory located in Library/Gems3/projects. More information on the GEMS folder structure can be found in Module 1.
- Open GEMS and choose the project in the **Equilibria Calculation Mode**. The user interface is shown in Figure 2.1. Panel 1 permits to create new records and run the program for calculations. Panel 2 gives you different calculation options.
- Choose the **Create a new record from scratch** from the menu in Panel 1 and fill the parameters listed in Figure 2.2
- In the **Open recipe dialog**, which can also be found in Panel 1, add phases, quantity and units as shown in Figure 2.3; Aqua (1000 g), HCl (0.1 M), NaCl (50 g), O_{2(g)} (1e-7) and K-feldspar (10 g).

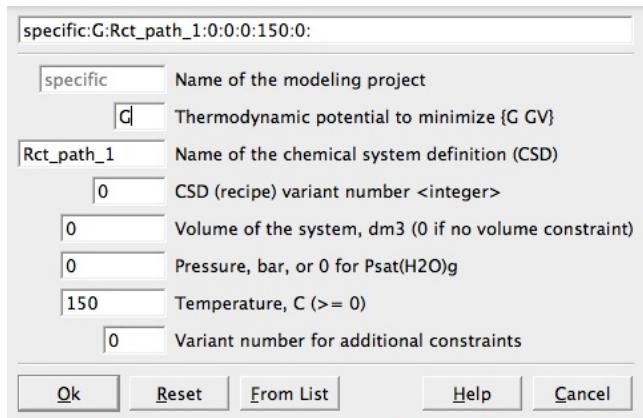


Figure 2.2: New record window. Select a name without spaces, a temperature and a pressure for your system. Note that a pressure of 0 corresponds to saturated water vapor pressure.

- Model the chemical equilibrium between 10 g of K-feldspar (microcline) and H₂O at 150 °C by pressing **Calculate BCC** followed by **Calculate Equilibrium** in Panel 1. Inspect the pop up window with pH, redox (eH) and phase proportions, then accept.
 - Determine the pH of this system as shown in the lower right of the main window (Fig. 2.4).
 - What is the pH of this system with 10, 20, 50 and 100 g K-feldspar? Change the amount of feldspar by clicking the **Open recipe dialog** followed by **Calculate BCC** and by **Calculate Equilibrium**. What minerals are stable with increasing pH?

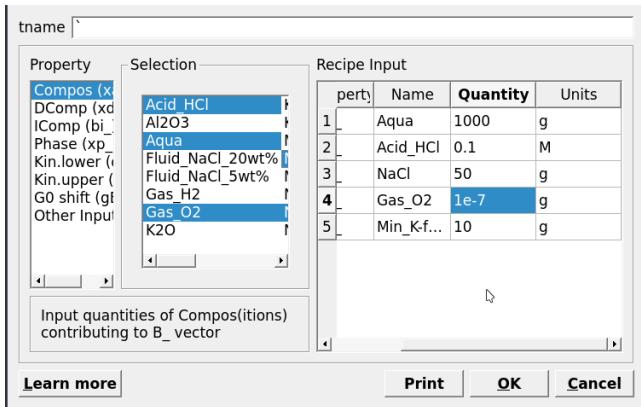


Figure 2.3: System recipe dialog.

- Finally, clone your existing Rct_path_1 chemical system by selecting it and choosing **Clone a new record from this one** in Panel 1 (Fig. 2.1). Change the name to Rct_path_2 and the temperature to 300 °C in the pop up window, and recalculate the equilibrium of this system.
 - Determine the pH of this system as shown in the lower right of the main window.
 - What is the pH of this system with 10, 20, 50 and 100 g K-feldspar? What minerals are stable with increasing pH?
 - Are there differences between the modeled system at 150 and 300 °C

2.2 Compute a titration model (Process, S mode)

The previous part of this tutorial showed you how to do individual SysEq calculations. What if you want to automate this process and calculate the equilibria of 10 to 100 g feldspar in steps and plot the results, i.e. a titration model? In the following we will see how to set up Process simulations.

- Select the **Process** option in Panel 2 (Fig. 2.1).
- Click **Create a record from scratch** in Panel 1 and select your parent chemical system SysEq calculated previously at 150 °C (Fig. 2.5).
- Name this process simulation “titration_150C” and use the **Process simulation code (S)** as shown in Figures 2.6) and 2.7).

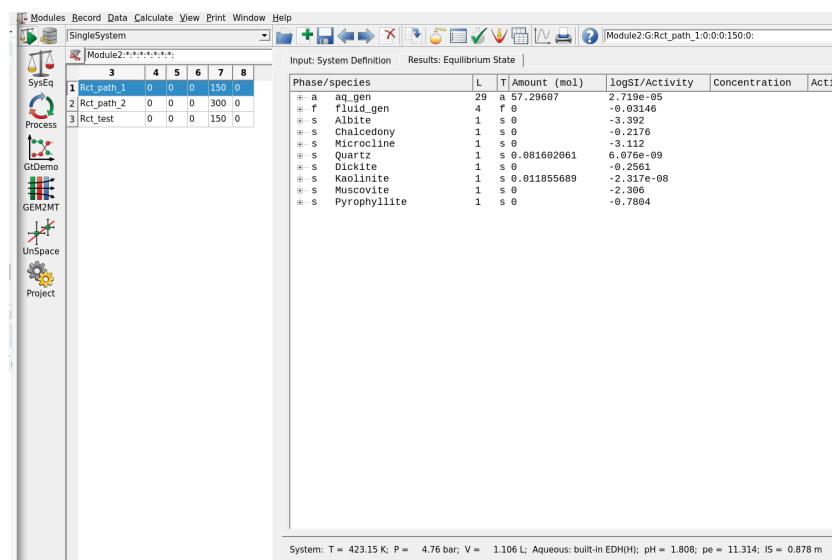


Figure 2.4: Results of the calculations, i.e. with 10 g K-feldspar added to the fluid.

- In the next window, choose a model (**titration cNu linear**), a mineral (**Compos**, **Min_K-feldspar**) and select the temperature (150 °C), pressure (0 for water vapor saturation P) and amount of mineral to be added (**iNu**: 10-250 g in 10 g steps) as shown in Figure 2.8. The parameters are: set **iTm** 1000, 1200, 1; set **iP** to 0 all fields; set **iNu** 10, 250, 10, corresponding to start, end, and step values.
- Select items to be plotted (**Scalars**: pH; Xa: Kaolinite, Pyrophyllite, Microcline, Muscovite, Albite and Quartz) as shown in Figure 2.9.
- Accept all the following dialogues. Then click on **Save this record to database** in Panel 1, which creates your new process simulation record. Then click on the calculator icon **Re-calculate and check record data** without displaying the graph.
- There is a tab menu with 3 important selections: **Controls**, **Sampling** and **Results**. In the **Controls** tab add a description of the modeling project (Fig. 2.10). In the **Sampling** tab change the script as shown in Figure 2.11 to choose as x-variable the amount of K-feldspar added (the process extent variable **cNu**).
- Click **Save this record to database**. Toggle to the **Results** tab to inspect your modeling results. Then click on the calculator icon **Re-calculate and check record data** and check what happens with

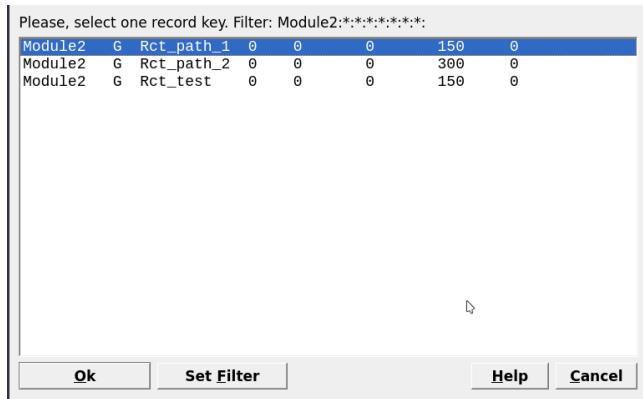


Figure 2.5: Select a parent chemical system ('SysEq') for modeling a 'Process'.

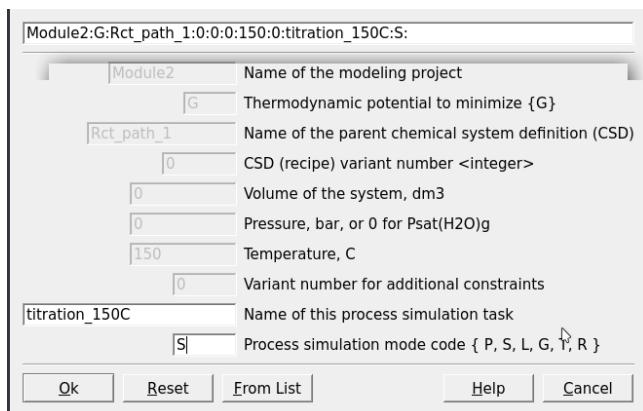


Figure 2.6: Name the 'Process' simulator and indicate the model type (note: the process type code names are described and changeable on the next screen as well).

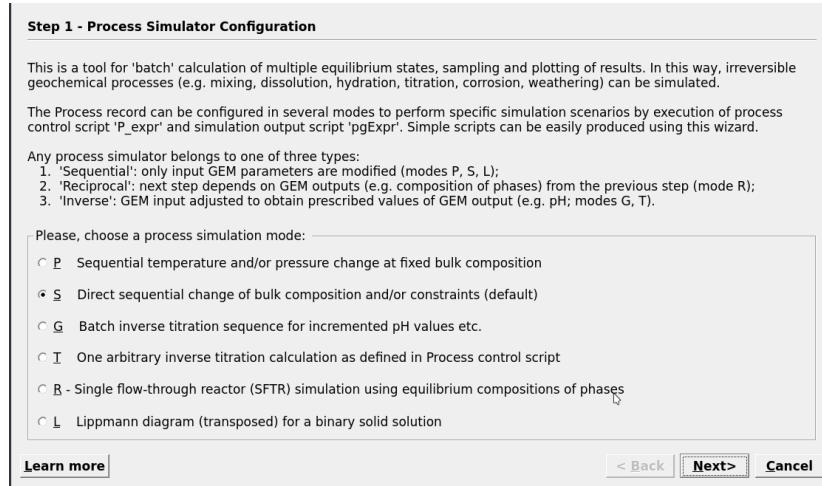


Figure 2.7: Window showing the different simulations types. Module 2 covers ‘mode S’ for titration or ‘mode P’ for cooling/heating models.

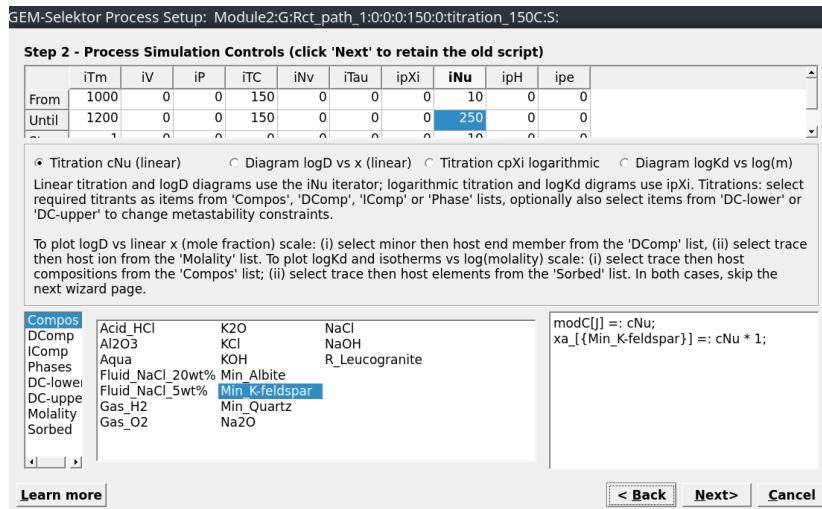


Figure 2.8: Set the parameters for the ‘Process’ simulation; Set ‘iTm’ 1000, 1200, 1; Set ‘iP’ to 0 all fields; Set ‘iNu’ 10, 250, 10.

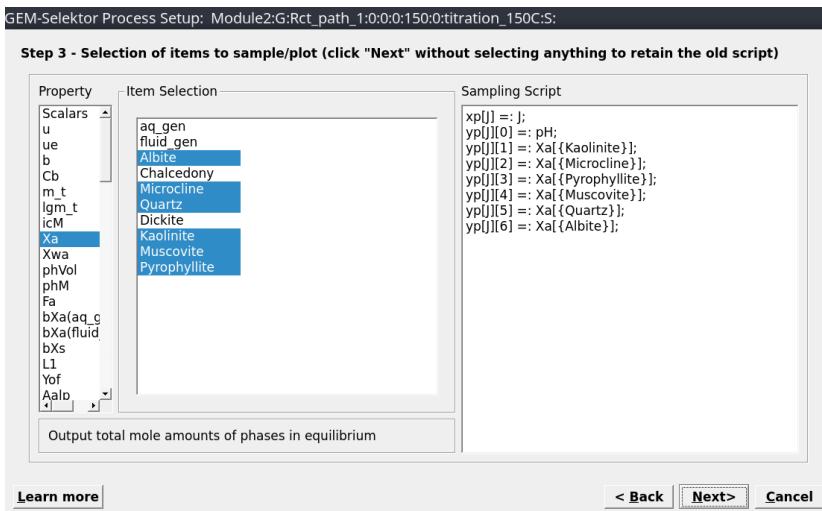


Figure 2.9: Choose the results to be plotted, including pH and mole minerals.

the column `xp`. You just assigned the `cNu` variable to the x-axis and GEMS registered it. If not, go back on the **Sampling** tab and check your script! Now lets inspect the results...

- How many grams of K-feldspar need to be added to get a constant pH and what is the value?
- Which mineral assemblages buffer the fluid pH and can pH ranges be distinguished?

2.3 Modify P-T of the feldspar reaction path

Now lets clone our record to calculate the exact same titration model but changing the temperature (T) to 300 °C and the pressure (P) to 500 bar.

- Clone your existing process simulation by selecting the existing record on the left and choose **Clone a new record**, then select your **SysEq** parent system calculated at 300 °C (Fig. 2.12). Accept all the following dialogues.
- In the **Controls** tab change the description of the modeling project and change the temperature to 300 °C and pressure to 500 bar to replace the starting and ending values (Fig. 2.13). Click **Save this record to database**.
- Switch the tab to **Results** and click the calculator icon **Re-calculate and check record data** to see how the pH values and moles minerals are changed by increasing the system temperature.

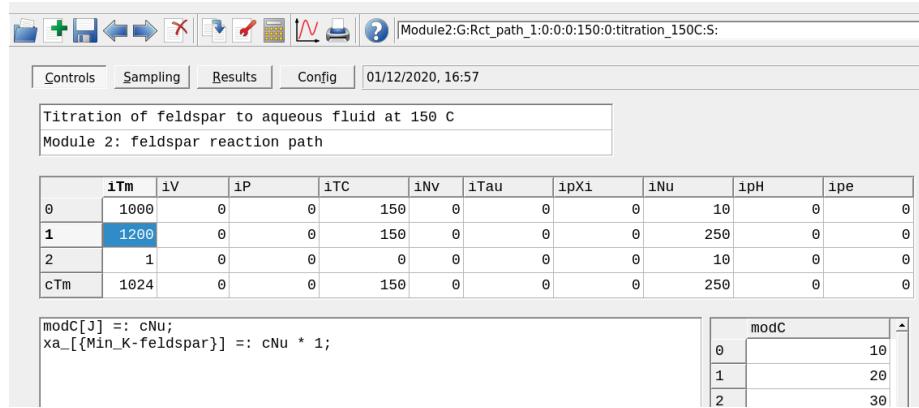


Figure 2.10: The ‘Controls‘ window showing the model conditions. The top dialog is used to add a comment and the script dialog can be customized. ‘iTm’ is used to set the record variable; ‘iP’ to set pressure and ‘iTC’ temperature; ‘iNu’ is the process variable, in this case the amount of feldspar.

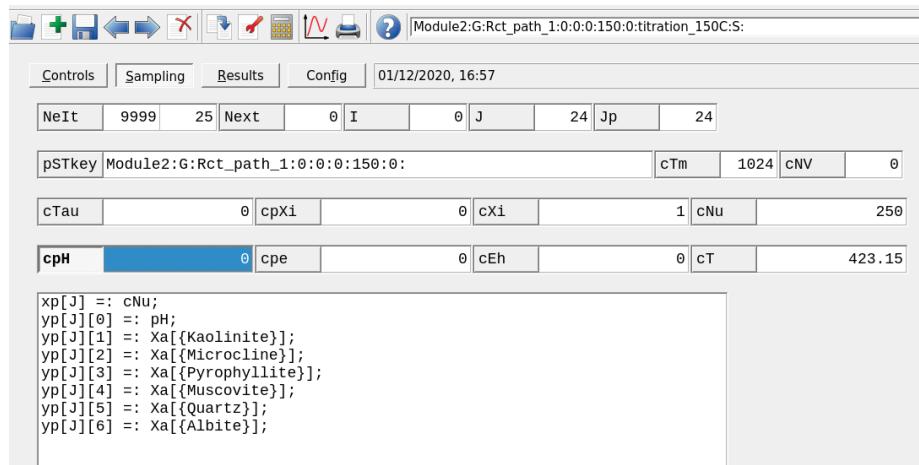


Figure 2.11: The ‘Sampling‘ window showing the x- and y-axes to be sampled. Make sure to change ‘xp[J]‘ to ‘cNu‘ which is the progress variable. Then click on a blank space to make sure the script window has been registered followed by ‘Save this record in the database‘ in the top panel.

- Toggle between both calculated process simulations at 150 and 300 °C on the left pane and compare the results.

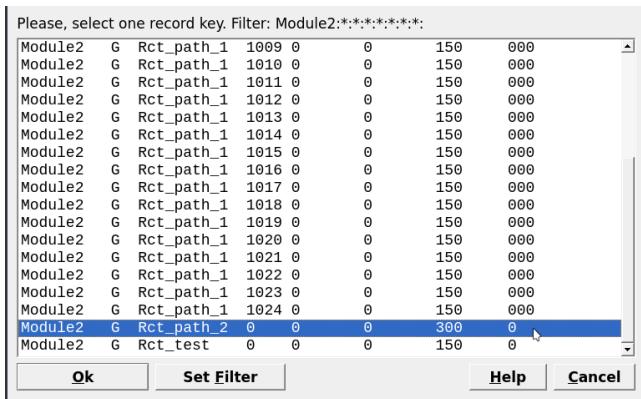


Figure 2.12: The ‘Sampling‘ window showing the x- and y-axes to be sampled. Make sure to change ‘xp[J]‘ to ‘cNu‘ which is the progress variable. Then click on a blank space to make sure the script window has been registered followed by ‘Save this record in the database‘ in the top panel.

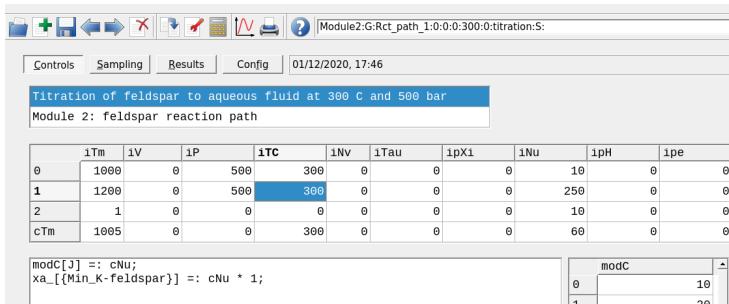


Figure 2.13: The ‘Controls‘ window showing a model set up at a different temperature and pressure.

2.4 Tweak and plot the results

So what are the main differences for the simulations at 150 vs. 300 °C? To make a better comparison lets fine tune our models and plot them!

- Select the process simulation you generated previously at 150 °C and in the **Controls** tab change the amount of K-feldspar to be added using 2 to 50 g in 2 g steps and save.

- Choose the **Results** tab and click the calculator icon **Re-calculate and check record data**. Click on the small **Plot data on Graph** dialog icon in Panel 1. The resulting graph should look similar to Figure 2.14. The plots indicate that different mineral assemblages buffer the fluid pH values.
- You can inspect which minerals by clicking the **Customize** button at the bottom of the plot and enter the values shown in 2.15, then click **Apply**. Click then on **Fragment** which will enable an inset view of your plot to have a closer look at the minerals. Clicking again **Fragment** zooms out to show the pH. It is also possible to do this with the mouse, but note that this will then overwrite the x-y-axis ranges you just entered manually.
- To label the lines on the plot simply drag the mineral names from the legend on the right into your plot.
- You can also switch on/off minerals or pH by toggling the corresponding fields in the laegend from 0 to off (or o-letter or 0-number keys on your keyboard). Now you should be able to reproduce the look in Figure 2.14. To save, simply click on **Save** at the bottom of your plot in the desired format (e.g. pdf, png, etc.).
- Now select the process simulation you generated previously at 300 °C and 500 bar. In the **Controls** tab change the amount of K-feldspar to be added using 5 to 125 g in 5 g steps, re-calculate and save. Try to tweak your graph to look like Figure 2.16.
- Figure 2.17 shows an alternative way to make a cumulative plot.
- You can now easily compare both feldspar reaction path models generated using the **Process** simulation in **S mode**!
 - The resulting reaction path at 150 °C is shown in Figure 2.14.
 - The resulting reaction path at 300 °C is shown in Figure 2.16.

2.5 Compute a cooling model (**Process, P mode**)

This part of Module 2 describes how to calculate the equilibrium between feldspar and the aqueous fluid at a constant mineral/fluid ratio but varying temperature. We will set up a cooling model from 150 to 300 °C in selected steps using the **Process** simulation in **P mode**. We will use knowledge gained until here. This part is quick so buckle up!

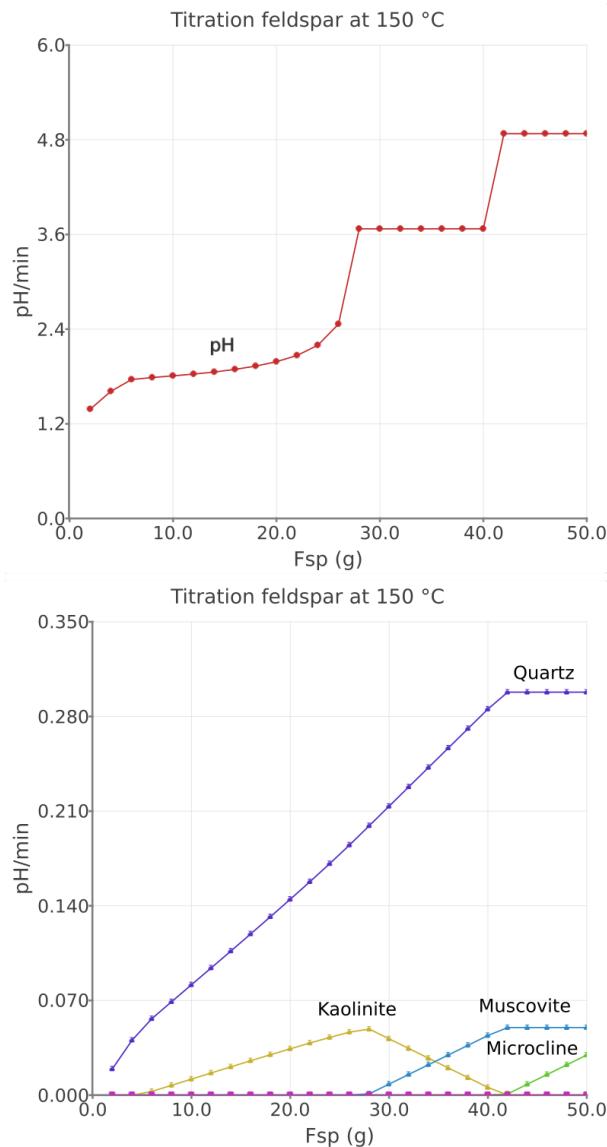


Figure 2.14: Simulated K-feldspar reaction path show pH and moles minerals in equilibrium with a saline aqueous fluid at 150 °C and saturated water vapor pressure.

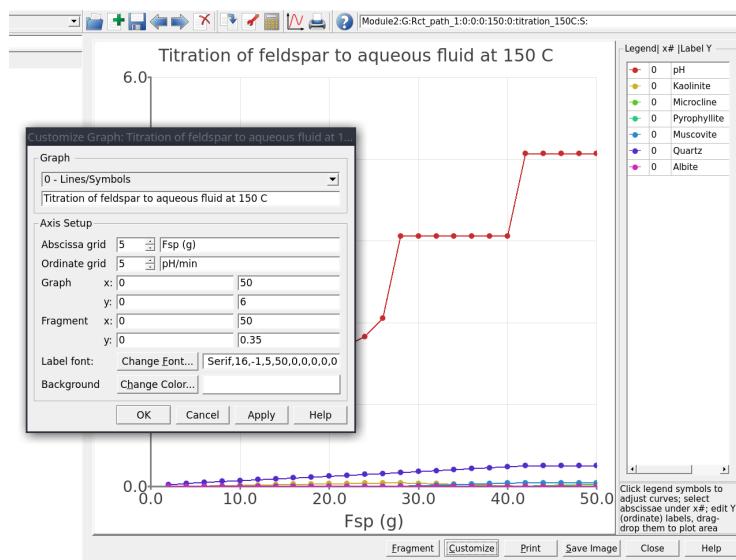


Figure 2.15: ‘Customize’ window showing options to tweak the plot. Here you can change the plot type, x- and y-axes, the font size, add labels and also the zoom-in feature by selecting x-y under Fragment. The right legend can also be turned on/off by toggling 0 to off (or using the o-letter or 0-number keys on your keyboard), and legend names dragged into the plot.

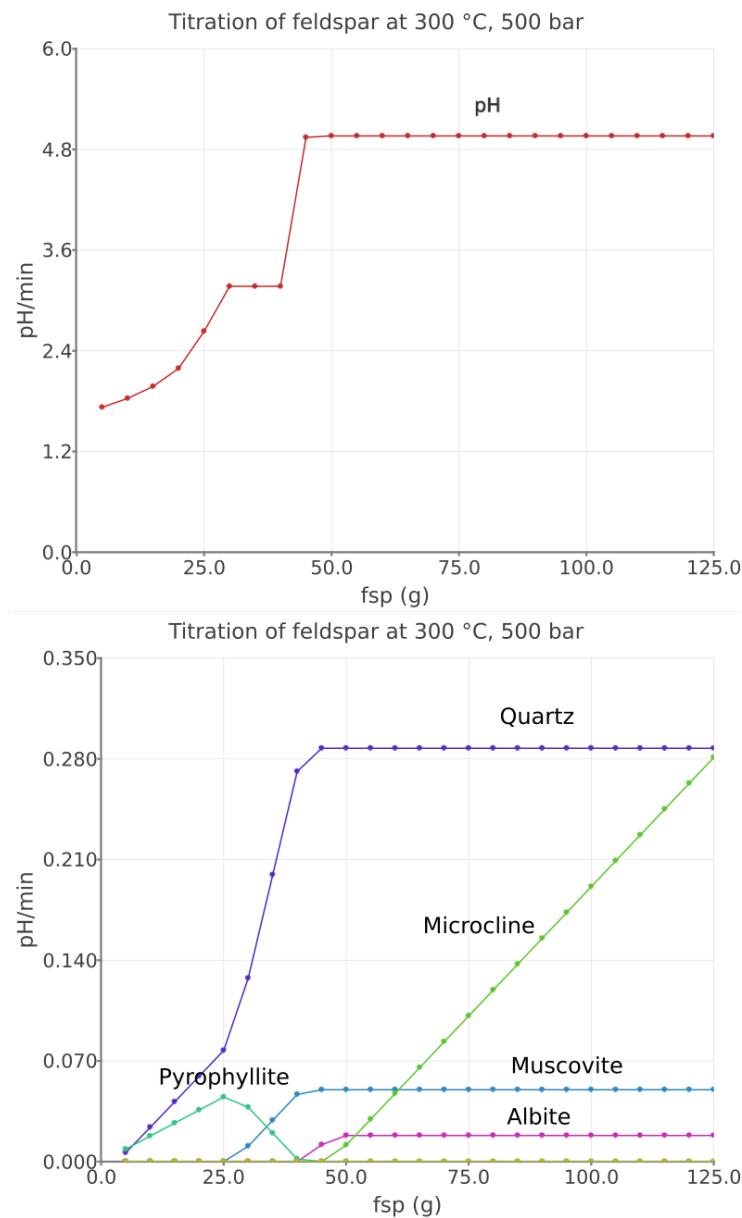


Figure 2.16: Simulated K-feldspar reaction path show pH and moles minerals in equilibrium with a saline aqueous fluid at 300 °C and 500 bar.

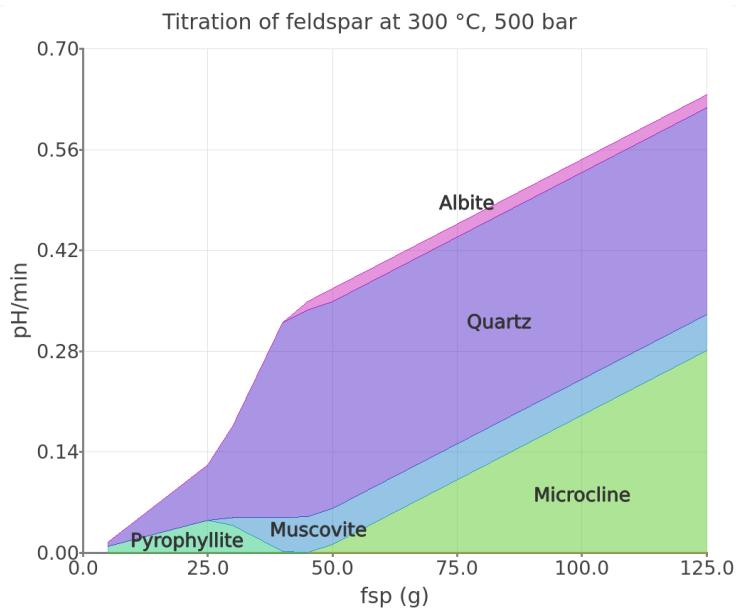


Figure 2.17: Simulated K-feldspar reaction path show pH and moles minerals in equilibrium with a saline aqueous fluid at 300 °C and 500 bar. To view this plot type choose the option ‘1- Cumulative’ plot in the plot ‘Customize’ window. Make sure to also switch off pH in the legend to only plot moles minerals.

- Create a parent system equilibrium record in **SysEq** simulation mode 2.4 by cloning Rct_path_2. Lets call this new record Rct_cooling, select 300 °C and 500 bar, and calculate its equilibrium.
- Switch to **Process**simulation mode and clone Rct_path_2. Select the Rct_cooling **SysEq** record (Fig. 2.18). Then call this new record Cooling_150-300C and select P for the simulation mode.
- In the **Controls** tab (or wizard step 2) select **No script**, set **iNu** to 0 and **iTC** to 300, 150, -5 as shown in Figure 2.19.
- The final step is to set the x-variable to temperature by modifying the script in the **Sampling** tab to **cTC** (Fig. 2.20). Save your record and re-calculate.
- Now you can plot and tweak your results to look similar to Figure 2.21).

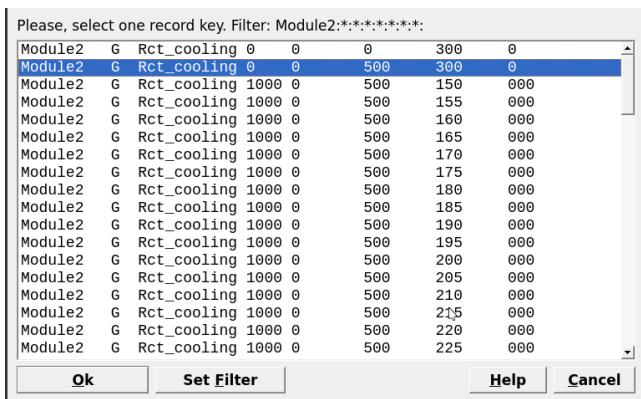


Figure 2.18: Select the parent record generated in ‘SysEq’ for your new ‘Process’ simulation.

2.6 Outcomes

Good job! In Module 2 you learned how to run and automate fluid-mineral equilibria simulations using the **Process** mode. You can now generate titration models in **S mode** or cooling models in **P mode**. You also know how to do plots in GEMS, tweak and export them.

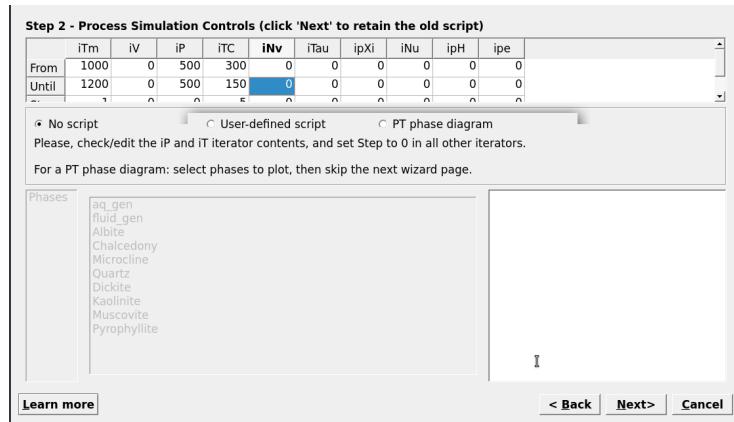


Figure 2.19: ‘Controls’ window showing the set up for a cooling model (no titration); select ‘No script’, set ‘iNu’ to 0 and ‘iTc’ to 300, 150, -5.

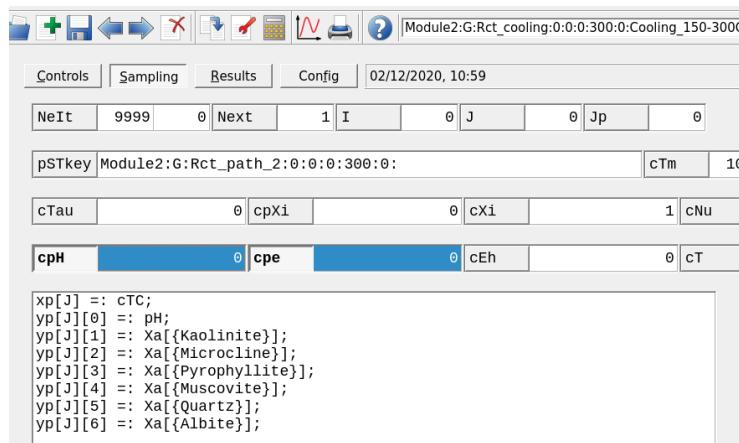


Figure 2.20: ‘Sampling’ tab window showing how to modify the x-axis to display temperature ‘cTC’.

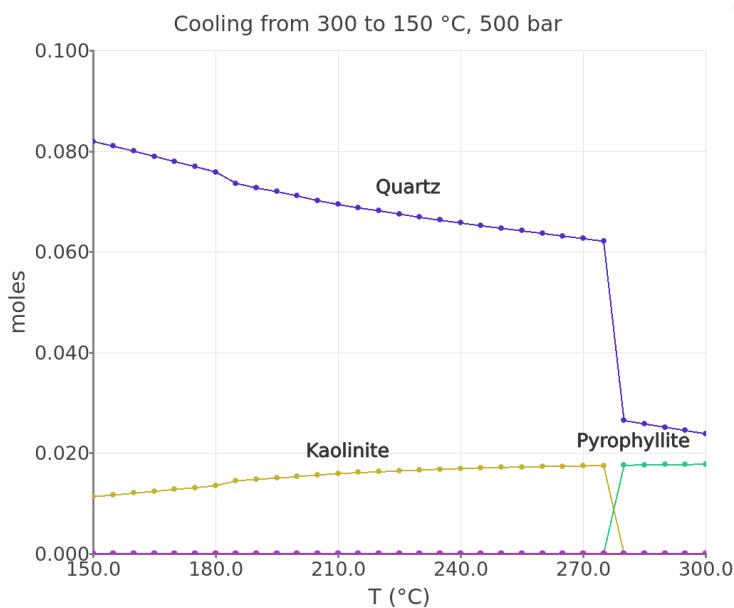


Figure 2.21: Cooling model showing the feldspar reaction path between 300 and 150 °C in 5 °C steps at a fluid/rock ratio of 100.

Chapter 3

Module 3

Work in progress...

Chapter 4

Module 4

Work in progress...

Chapter 5

Module 5

Work in progress...