VolcDeGas: A program for modelling hydrogen isotope fractionation during degassing of rhyolitic melts. Supplementary Material

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This supplementary information contains: 1) a detailed description of goodness-of-fit methods and formulae; 2) additional VolcDeGas model simulations represented by three separate figures (Supplementary Figures S1–S3), in addition to two images (Figure A1 and A2) of the Graphical User Interface (GUI); and 3) a "Manual" for VolcDeGas that provides general user information and tips at the end of this document.

1 Goodness-of-fit psarameters

Three goodness-of-fit factors are calculated in VolcDeGas to provide objective information about the best-fit of the different model trends to natural δD-H_2O data.

One factor is the Coefficient of Determination (R^2), which describes the proportion of the variance in the dependent variable that is predictable from the independent variable (linear least squares regression model). R^2 values in addition to giving a measure how the data deviates from a model curve, R^2 also displays if the data points are in a relationship to each other, that is, if they form a specific trend. In VolcDeGas, an R^2 of 1 (maximum value) implies that the dependent variable can be predicted without error from the independent variable. The larger the R^2 is, the more the variability is explained by the linear regression model. The formula of R^2 is:

$$R^2 = 1 - \frac{\sum_i (y_i - f_i)^2}{\sum_i (y_i - \bar{y})^2} \tag{S1}$$

where y is the observed data (here natural data), f is the predicted or modelled data, and $\overline{y}$ is the mean value of the observed data.

Because R^2 increases when more explanatory variables are added, the adjusted coefficient of determination R^2_{adj} is utilised to account for this:

$$R^2_{\text{adj}} = 1 - (1 - R^2) \times \frac{n-1}{n-p-1} \tag{S2}$$

Here, the n describes the number of data points and p is the number of explanatory variables.

A third goodness-of-fit factor, the Root-mean-square error (RMSE) also gauges the best-fit between model and natural data, and is automatically calculated in VolcDeGas. RMSE measures the numerical differences between the model and observed (natural) data, and estimates how concentrated the data is around the line of best fit.

The formula of RMSE is:

$$\text{RMSE} = \sqrt{(f-y)^2} \tag{S3}$$

where y is the observed data (natural data) and f is the modelled value.

2 Additional VolcDeGas simulations

Additional VolcDeGas simulations are shown in Figure S1, S2, and S3.

3 VolcDeGas instruction manual

3.1 General information

The code of the program VolcDeGas has been written in MatLab R2018a but is fully downwards compatible to at least MatLab R2012a. It requires the MatLab Signal Processing-, as well as the Statistics and Machine Learning Toolbox. Yet, the compiled self-installer does not require MatLab at all (only a Windows system).

Required Matlab files are:

- `VolcDeGas.m`,
- `VolcDeGas.fig`;
- `VolcDeGasoptions.m`, and
- `VolcDeGasoptions.fig`.

These files should be placed in a folder which MatLab can access (MatLab path). It is accessed by typing `VolcDeGas` into the workspace. Alternatively, if

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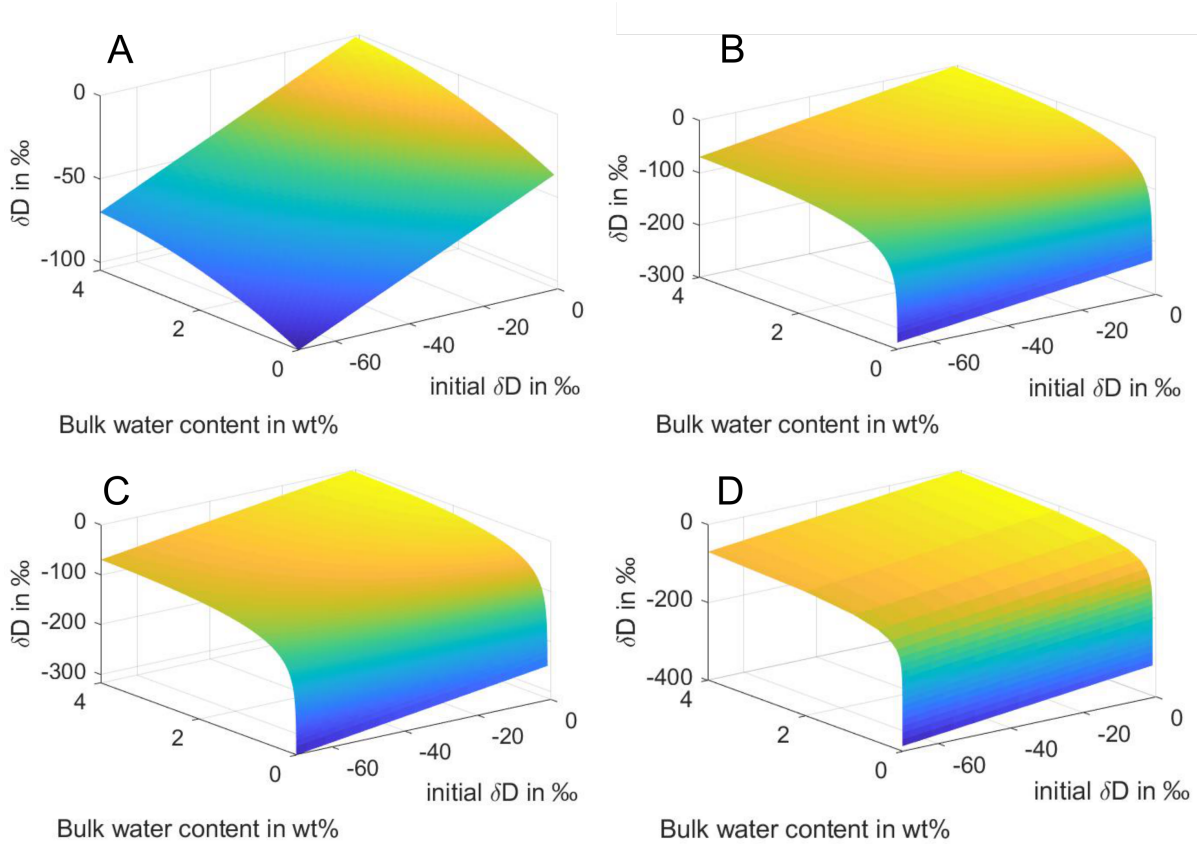

Figure S1: 3-D plots of VolcDeGas simulations of different one-stage systems utilising water speciation values of Castro et al. [2012] for the alpha factors calculations. [A] 3-D graph representing a simulated closed-system degassing case. The slightly curved trend in the direction of lower bulk water contents is due to the alpha factor changing over the trend of degassing. [B] 3-D graph demonstrating the open-system degassing case. This is a prime example of open-system degassing causing strong depletion of deuterium at lower water content. [C] 3-D graph demonstrating a batched-system degassing case. With the small step size (0.001 wt%), the batched system mimics the open system behavior and leads to even stronger at lower water content. [D] 3-D graph showing the batched-system degassing with variable step-sizes. The percentage of H_2O loss at each step is set to 50%. At high H_2O contents where step size is bigger, the model mimics closed-system, while at lower H_2O contents the open system is imitated.

a Microsoft system is used, there is also the possibility of installing the compiled program by invoking the `VolcDeGas.exe`.

3.2 Code description

The program of this work called `VolcDeGas` utilises a GUI to easily import data sets and change parameters. A GUI with its buttons is required to calculate the many different systems involved in degassing. Hints on each button or field are explaining them in a straight forward as well as giving additional advices. As a result, the user can quickly and user-friendly change and calculate the different best-fit one-, and two-stage degassing histories in relation to their natural data, either manually "by-hand" or automatically by the program. In case of the automatically calculations, the best-fit is decided by the help of the lowest RMSE error. For these calculations, the user only has to set the confining parameters which should be set broader to produce more possible graphs. Particularly the initial δD values, which are responsible for the different parallel graphs are recommend to extend far (e.g. −80 ‰ to −20 ‰ with 1 ‰ as interval). Extensive testing of different rhyolitic systems showed excellence performance of the different program parts, especially the automatically computation comfortably detects the best-matching degassing histories.

3.3 User advice and code explanations

Firstly it is important to press the button `Clear workspace for next run` and to close all figures, whenever a new system is calculated. Especially if the user changes the system from a system with constant step size to a system with variable step size or *vice versa*. This does not include two-stage systems in a way as the user may start with a closed system and then sets the

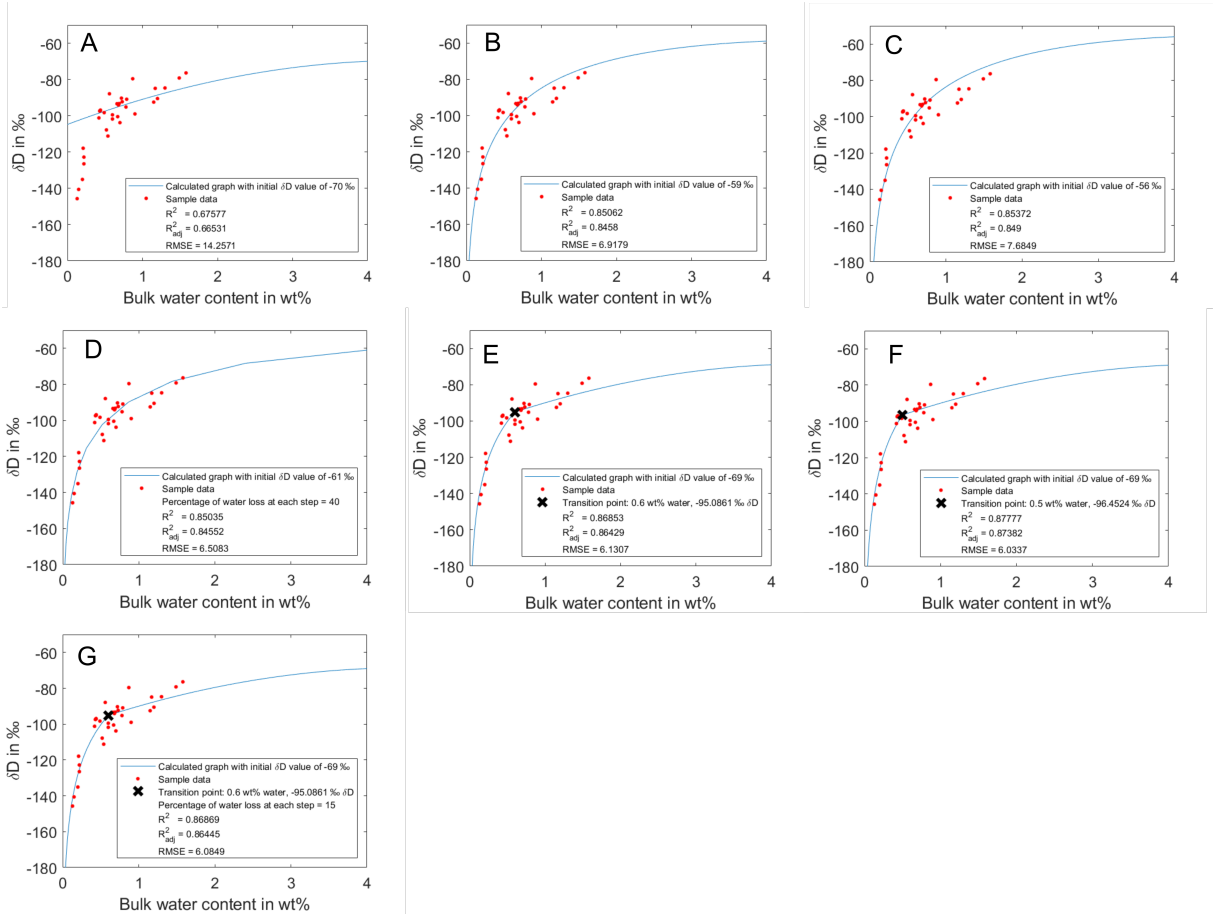

Figure S2: 2-D graphs computed by VolcDeGas which display the best-fit solutions to available natural δD-H_2O data of the 2008 Chaitén eruption [Castro et al. 2014]. The alpha factors used to simulate these graphs are calculated using the hydrous speciation data of Castro et al. [2012]. The initial bulk water content is set to 4 wt.% and the standard step-size to 0.001 wt.% H_2O. [A] Best-fit closed system calculation. As shown, the natural data and the simulated graph do not match well, which is also statistically indicated by the high RMSE value and the low R^2. [B] Modelled best-fit open-system degassing trend illustrating a better fit to the natural data than in the closed-system ([A]; note the smaller RMSE and higher R^2). [C] Modelled best-fit batched-system trend with a constant, small (0.001 wt.%) step size, demonstrating a relatively good reproduction of strong deuterium depletion at low H_2O contents. [D] Modelled best-fit batched system with variable step size (40 % H_2O loss at each step). The goodness-of-fit to natural data is good and comparable to previous models [B]–[C]. This model, does however, demonstrate the lowest RMSE of all one-stage systems, and therefore confirms it as the best-matching one-stage degassing system. [E] Two-stage degassing simulation comprising closed-to-open system behavior. The best-fit transition point at 0.6 wt.% H_2O marks the change over between degassing styles. This graph shows that the two-stage system fits sample data better than any of the one-stage systems (as reflected by significantly lower RMSE). The simulation also demonstrates a relatively good matches between the closed-system segment at high H_2O content, and open-system segment for the late-stage history at lower H_2O contents. [F] Two-staged, closed-to-batched degassing simulation. Step size for batched segment is constant and small (0.001 wt.%). Here the fit is good with an RMSE which is slightly lower than the closed-to-open system case [E]. The best fit transition point is 0.1 wt.% lower (at 0.5 wt.% H_2O) than in the previous simulation. [G] Closed-to-batched degassing system with variable step size (15 % H_2O loss at each step). There is no noticeable difference in the RMSE value compare to the previous simulation involving a batched system with fixed step size [F].

transition point for the second stage. Here, the `Clear workspace` button only has to be used after the user has finished this two-stage system as well as also exporting the calculated data to excel or changing the font size.

This program has been written in a user-friendly manner. That is, that not only hints, which appear by hovering over specific buttons are giving information, but also error messages are applied. In most cases however if-loops prevent errors or crashes of the program especially if variables are missing as they were not set, or if the user is utilising the program in a strange order. Also, at extensive calculations a wait bar is im-

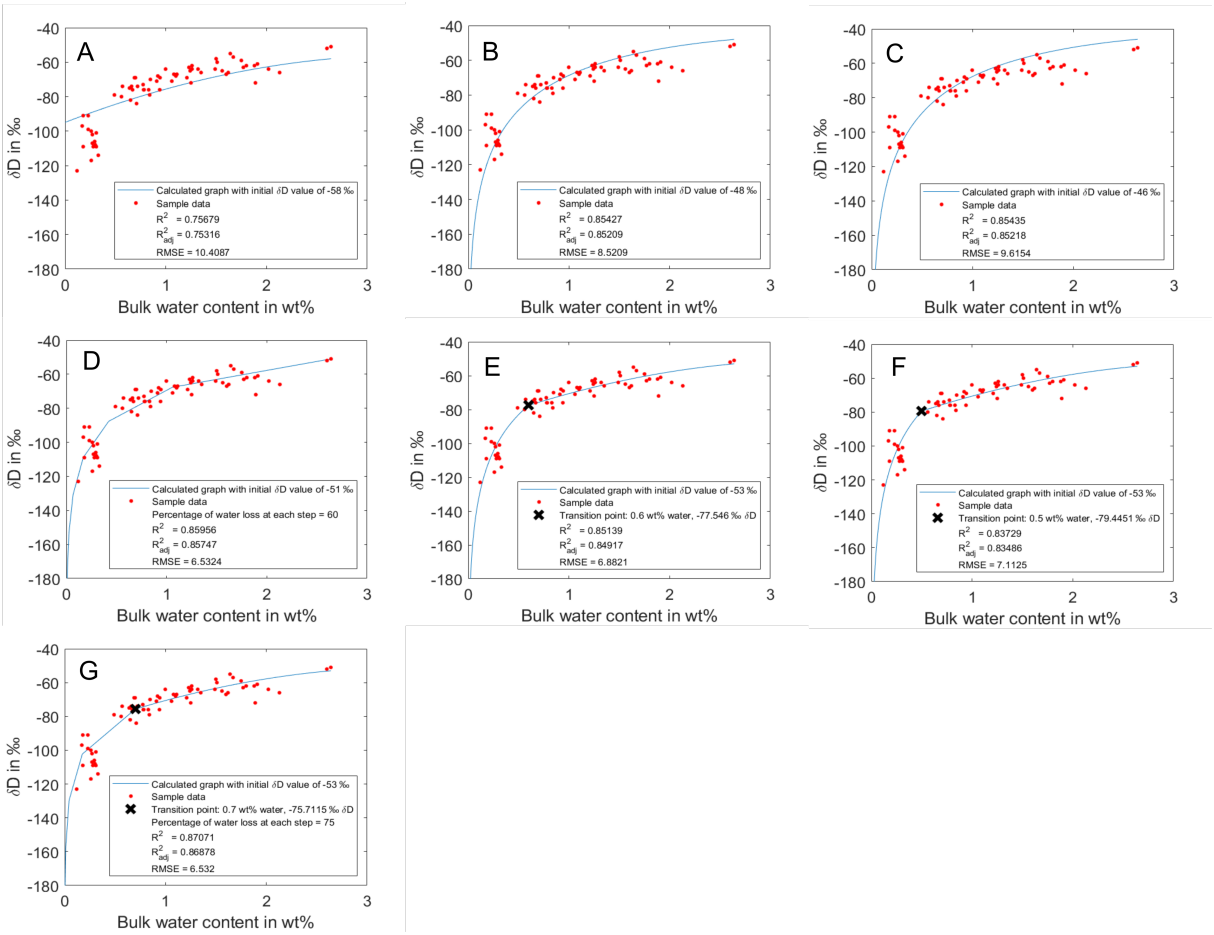

Figure S3: Graphs of the best-fit `VolcDeGas` simulations of various degassing systems to the 1340 C.E. Mono Craters eruption, the data of which come from Newman et al. [1988]. The calculations are conducted with alpha factors established by H_2O speciation data of both Newman et al. [1988] and Barnes et al. [2014]. The most H_2O-rich clast (2.64 wt% H_2O) is set as the initial bulk H_2O content and unless otherwise noted, the common step-size is set to 0.001 wt% H_2O. [A] Best-fit simulation of the closed-system degassing. The goodness-of-fit here is poor (very high RMSE); considered collectively, the dry and wet samples do not match the graph, however the closed system does seem to mimic the trend of the H_2O-rich samples. [B] Graph showing the best-fit open-system degassing simulation. This system exhibits a better fit than the closed-system but the general fit as well as the RMSE are not ideal, especially since the system cannot closely mimic the high H_2O content samples. [C] Diagram of the best-fit batched system to the Mono Craters data. Constant small step (0.001 wt.%). Fits to the data are only slightly less accurate than in the open-system case, as proven by the marginally higher RMSE, reflecting that the high-H_2O content samples are not accurately portrayed by the calculated graph. [D] Best-fit batched-system with variable step-size (60 % H_2O loss at each step). In contrast to all other single-stage models, this system displays the lowest RMSE as well as a clearly better fit to low and high H_2O content samples. Moreover, the δD value and water content of the starting point regarding the simulated degassing history matches the initial values of the wettest sample (2.64 wt.% and 51 ‰ δD), perfectly. [E] Two-stage, closed-to-open system model of the Mono Craters eruption products. This system displays a good fit to the samples at high-, as well as low - H_2O contents, which confirms a two-stage systems is a reasonable model for Mono Craters [e.g. Newman et al. 1988]. Moreover, the fit here is noticeably better than in the one-stage systems, except perhaps for the batched-degassing system with variable step-size, as this appears to mimic the natural degassing trend slightly better. [F] Simulation of a closed-to-batched degassing system with fixed step size (0.001 wt.%). In contrast to the closed-to-open system [E], the fit is slightly poorer which is reflected in the lower RMSE. [G] Simulation of a closed-to-batched degassing system with variable step-size (an increment of 75 % of H_2O lost at each step). This system shows the best-fit of all simulated degassing systems (lowest RMSE). As the model suggests, a a repetitive pulse-like degassing mechanism whereby the size of pulses decreases with time is could be consistent with observed rhyolitic activity, comprising the protracted explosive-to-effusive transition and continuous decline of explosive power through time (e.g. at Chaitén).

plemented to inform the user that the program is still running and about the progress of the calculation.

To input user data an excel sheet is required to be prepared. If optional water speciation data (Button: `Input own speciation values ...`) is available the first row has to only contain wt.% of total water content and the second row wt.% of molecular water. In case of natural δD data (Button: `Input excel`), the first row has to include the wt% percent bulk water content and the second row the δD value. Although in the optional case here, the alpha factor is calculated without using the temperature, the field for temperature has to be filled out (random number is sufficient).

To allow the program to work properly, if the bulk water content field (From) which is the final bulk water content, where degassing calculations ends, is set as 0 the program overwrites this value with a value close to 0 (0.00001). As lower values can be calculated without noticeable more process time, it is advisable to write 0 in this field.

Since the step size influences on closed-, and open systems are negligibly, bigger step sizes (interval) should be avoided as they lead to an edged graph and prevent the effective automatically computations (Button: `Let program calculate the best matching degassing histories`). As a result, the step size, especially in auto calculations should be set to a small value like 0.001. As the batched system with variable step size calculates its own step size values, the only system heavily influenced by the set step size, is the batched-system with constant step size. For the automatically calculation it is also important, that the proposed transition point (in the field `Set most likely transition point (default 0.6 wt.%)`) is set lower than the natural data. Else, the program cannot calculate a best-fit closed system, which is the base for the two-stage calculations. Thus in the case of too little natural data, the user should detect the best-fit by hand, with the manual program part which is mainly accessed through the second GUI window `VolcDeGasoptions`. In this window some additional features like saving the calculated data as a excel sheet `Create excel with calculated data`, or several layout functions can be executed.

In certain fields, a default value is set if the user does not enter a value. It is recommend to use these default values, as they are showing the most positive results for numerous tested systems.

This program was written so that it should not crash, however if it does or a bug appears press `Clear workspace for next run` and close all figures.

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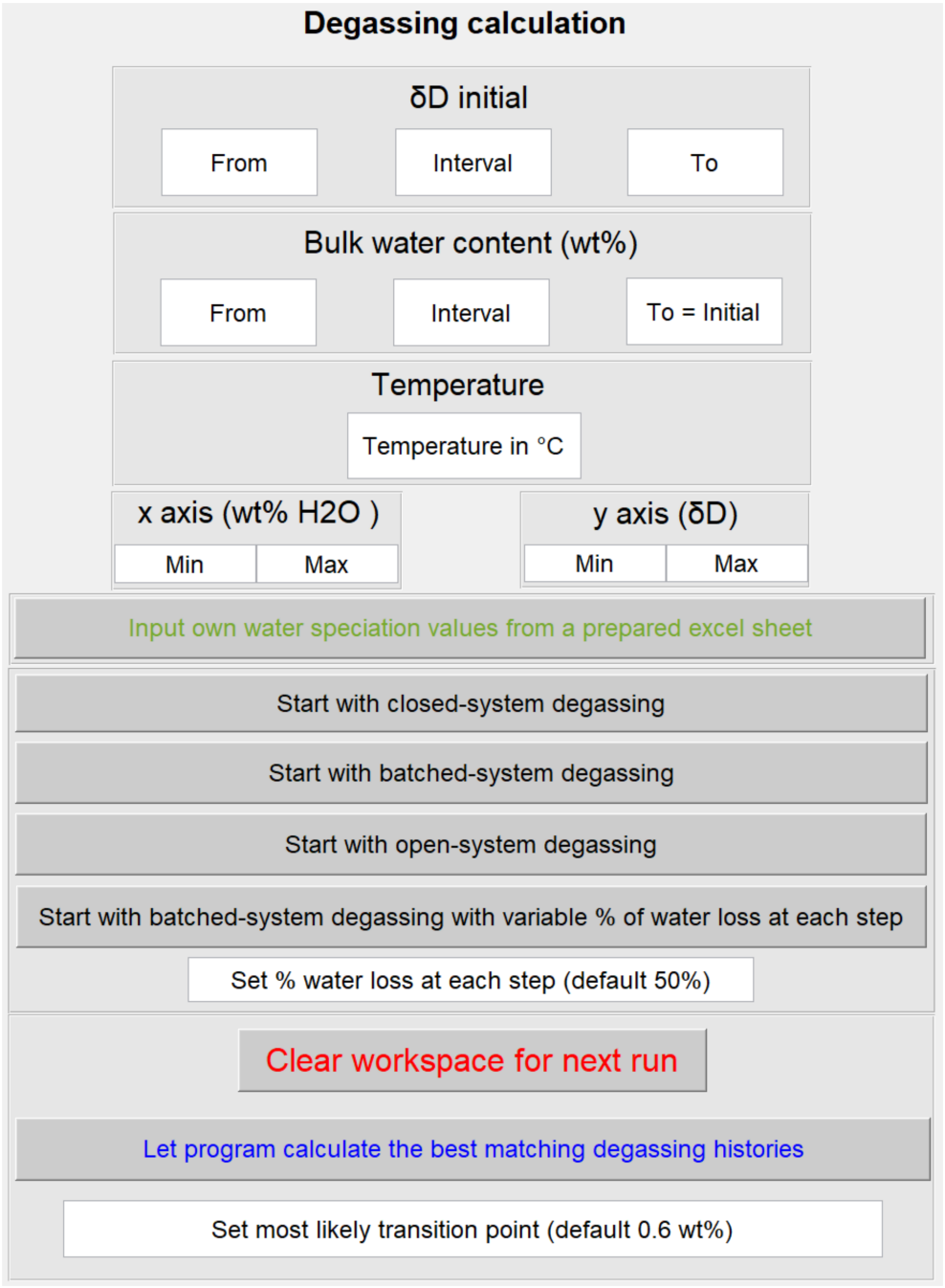

Figure A1: `VolcDeGas` Graphical User interface (GUI) indicating inputs of the main variables and function buttons.

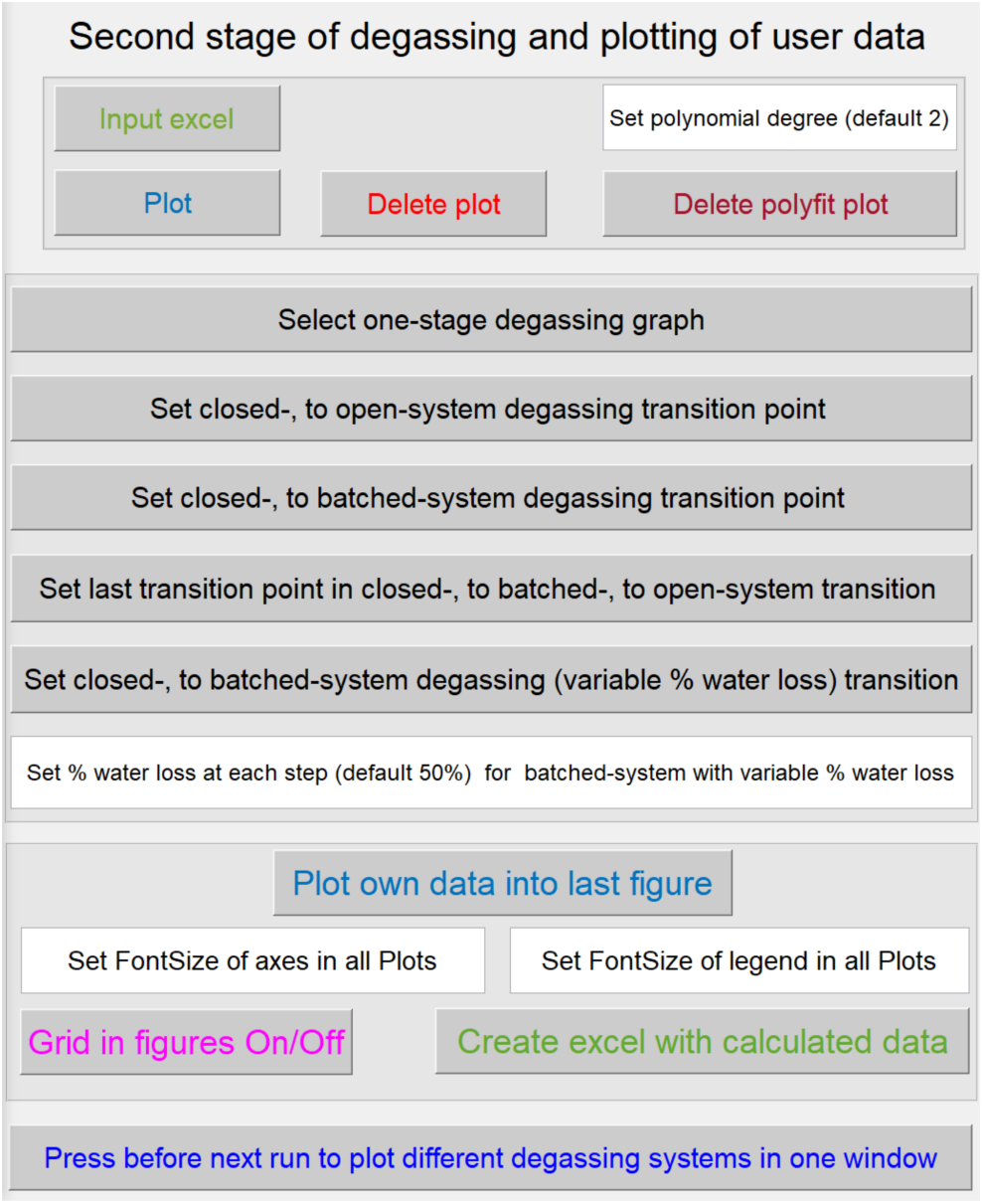

Figure A2: VolcDeGas Graphical User interface (GUI) showing the secondary window which gives additional layout functions and second-stage calculation buttons.