

Local Minima in Geochemical Reaction Optimization Problems

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Abstract

It is increasingly popular to optimize geochemical reaction models to fit lab or field data. Performing these optimizations is often technically difficult due to the highly correlated nature of the parameters and the common presence of local minima in the optimization error surface. However, there are simple techniques for recognizing when minima will occur and ways to remove many of minima from the optimization problems. If the cause of the minimum is known and the sum of the square weighted residual (SSWR) is the measurement of error, then adding terms to the SSWR and restating the optimizations goals may remove the minima. The SSWR term might also need to be redefined to include quantifying the error in more dimensions. Also, one of the best tools for understanding where minima might occur is through creating phase diagrams of the parameter space so that you can understand phase equilibria and where parameters may change or be static.

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Key Points:

- Many local minima in geochemical modeling are predictable and avoidable.
- Redefinition of the model residual error is often beneficial.
- Phase diagrams provide a valuable insight into where minima occur.

Abstract

It is increasingly popular to optimize geochemical reaction models to fit lab or field data. Performing these optimizations is often technically difficult due to the highly correlated nature of the parameters and the common presence of local minima in the optimization error surface. However, there are simple techniques for recognizing when minima will occur and ways to remove many of minima from the optimization problems. If the cause of the minimum is known and the sum of the square weighted residual (SSWR) is the measurement of error, then adding terms to the SSWR and restating the optimizations goals may remove the minima. The SSWR term might also need to be redefined to include quantifying the error in more dimensions. Also, one of the best tools for understanding where minima might occur is through creating phase diagrams of the parameter space so that you can understand phase equilibria and where parameters may change or be static.

1 Introduction

Geochemical models, particularly those built on field data, often contain a large number of unknowns. While model creators can constrain some of these parameters with values taken from the literature, it is common for lab derived rates and values to differ significantly from those observed in the field due to a wide array of factors and controls (Anbeek, 1993; Li et al., 2007; Maher et al., 2006; Malmström et al., 2000; Steinwinder & Beckingham, 2019). Also, most data simply do not fall along the nice clean trends we would prefer due to varying flow paths, measurement error, etc. These discrepancies and difficulties lead to the introduction of optimization algorithms when simulating geochemical processes or deriving kinetic rates.

Unfortunately, optimizing geochemical or reactive transport models can be a complicated problem. Optimization traditionally seeks to minimize a measurement of error, such as the sum of the squared weighted residuals (SSWR) (Fitzpatrick, 1991), which describe the distance between observations and simulated output, but over that range of parameters the measurement of error frequently

has local minima or flat areas that make optimization difficult regardless of the method used (Wolpert & Macready, 1997).

The purpose of this work is to show how local minima on the error surface can be removed in certain circumstance. In many cases, these minima are not random and will disappear if the optimization problem is reframed or the measurement of error is redefined. Doing this requires a knowledge of what is causing the local minima and the different phases that occur across the parameter space.

2 Materials and Methods

There are three scenarios presented in which local minima and flat areas occur on the SSWR surface. These scenarios are simple models constructed to illustrate the causes of minima when performing an optimization. The base simulations ran in X1t and React and Act2 calculated the phase diagrams (Bethke & Farrell, 2021) using a pre-existing thermodynamic database (Wolery, 1992).

The first scenario simulated a front of Br^- flowed through a 10 cm system similar to an experimental core-flood (Figure 1a). The “observations” are values taken from the simulation where two pore volumes are pumped through the system with random error added to the Br^- concentrations mimicking analytic error and flow through a heterogeneous system. The SSWR is the squared difference of the “observation”, *Obs*, and the simulated value, *Sim*. The weight, *W*, used here is the maximum modeled value but analytic error of the observation is often used (Hill & Tiedeman, 2007).

$$SSWR = \sum (Obs - Sim)^2 / W^2$$

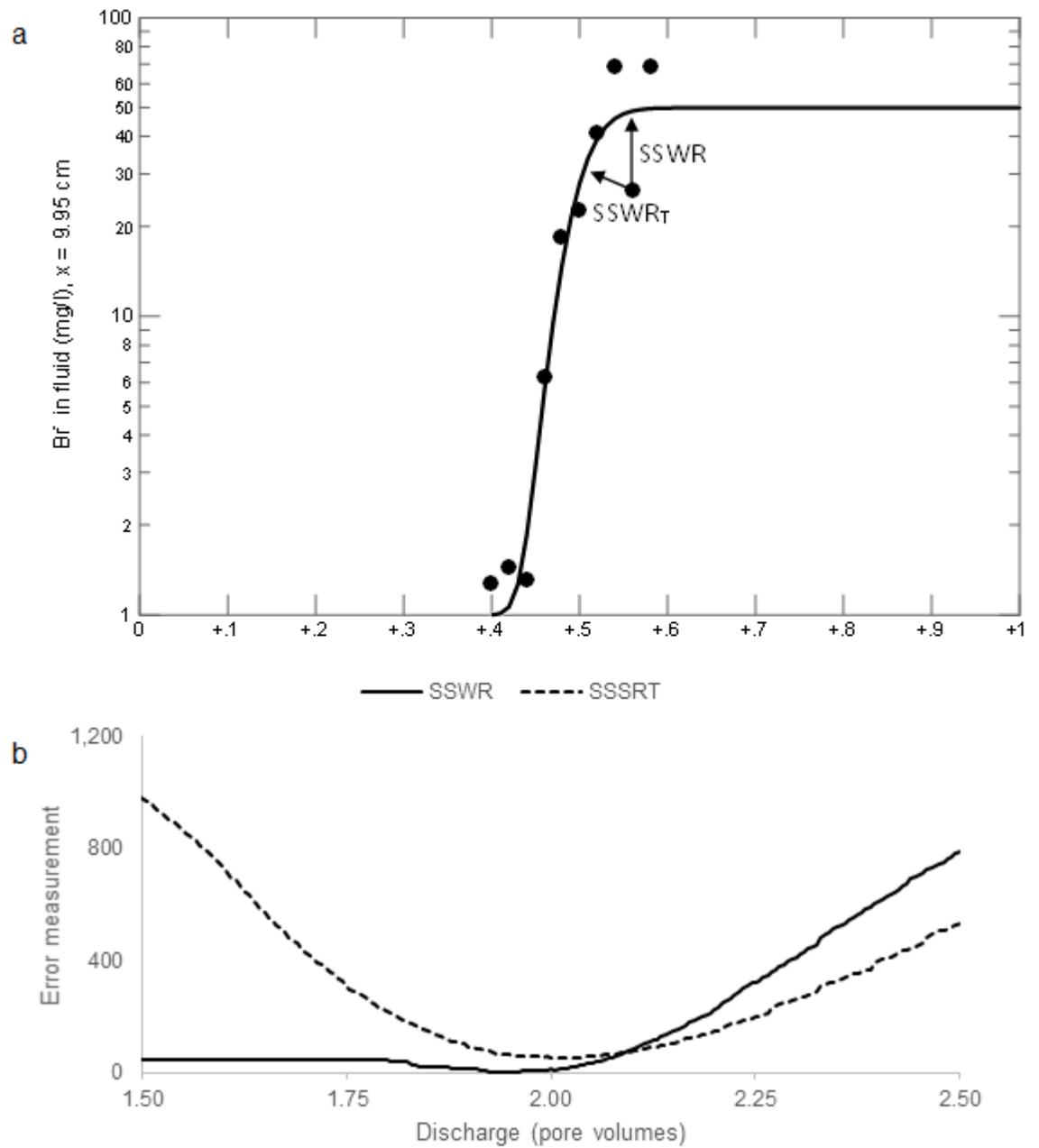
The second scenario is the addition of pyrite to a kilogram of water. The pyrite maintains equilibrium with the solution and initially dissolves. The SSWR used as if trying to match Fe and S concentrations and “observation” being chosen as the concentrations after 10 mg of pyrite was added.

Scenario 3 is a simple titration of an acidic solution with Fe and S from an initial pH of 4 to 7.5.

3 Results

3.1 Scenario 1

Using the standard SSWR for this scenario is problematic due to a flat area and local minimum. For low discharges, it creates a flat area which reflects that the Br front not reaching the outlet for those values. There is also a local minimum at 1.9 pore volumes and a global minimum at 1.95 pore volumes (Figure 1b). The local minimum was caused by the model exactly matching one of



data points as the front moved through.

To remove these problems from the optimization, we define the SSWR_T as

$$SSWR_T = \sum \min \left\{ (Obs - Sim)^2 / W^2 + (T_m - T_o)^2 / T_w^2 \right\}$$

where T_m is the time step of the model, T_o is the time of the observation, and T_w is a weight ideally a reflection of sampling error such as the time needed to take a sample. The SSWR measures the distance between the model and the observation only in the concentration dimension while the $SSWR_T$ finds the minimum distance in between the observation and the modeled line in both dimensions (Figure 1a). In Scenario 1, the $SSWR_T$ has a minimum is at 2.005 which is closer to the expected value and has no flat areas or local minima. A similar measure of error can be constructed in problems where the second dimension is distance instead of time.

3.2 Scenario 2

There is a large flat area over a significant portion of the parameter space in this scenario (Figure 2). Here, the flat area is caused by the fluid equilibrating with the mineral phase. Adding additional amounts of pyrite has no effect on the aqueous chemistry once this saturation point is hit. An additional term to the SSWR removes this flat area:

$$SSWR_{Py} = \sum (Obs - Sim)^2 / W^2 + Py^2 / W_p^2$$

where Py is the amount of pyrite added to the system and W_p is a weighting term. The additional term changes the optimization from “how much pyrite needs to be added to match the observations” to “what is the least amount of pyrite added that match the observations”. The additional term does offset the global minimum, but that error is minimized by adding the weight term, 75 mg here, to ensure the pyrite term is minimal compared to the SSWR outside of the flat area. A similar problem arises in matching kinetic rates for minerals when the rate becomes so fast the solution reaches equilibrium. In this case, an optimization strategy may be searching for the slowest kinetic rate that matches the data.

[CHART]

Figure 2. Measurement of error between the amount of Fe and S in solution versus the desired amount from Scenario 2.

4.3 Scenario 3

A similar effect to that of Scenario 2 is seen due to aqueous phases in Scenario 3 (Figure 3). Here the iron and sulfur initially remain constant as the pH of the system changes because the stable phase in the system is aqueous instead of a mineral. An optimization that simply relied on the elemental analysis of the aqueous phase would fail over any part of the parameter space that did not have a mineral phase present. This problem could be avoided by including Eh or ratios of oxidation states such as Fe^{2+}/Fe^{3+} and H_2S/H_2SO_4 . In this case, a simple examination of the parameter space through the creation of a

phase diagram allows for recognition of problematic domains before optimization begins.

5 Conclusions

Local minima are inherent in geochemical optimization problems. However, their occurrences are often predictable and the result of geochemical processes. Some minima can be removed if the measurement of error is recalculated to take into account all of the dimensions that are part of the problem and some can be removed if the optimization problem is recast in a way similar to using prior information (Cooley, 1983). Finally, understanding the phases present over the breadth of a parameter space by building the relevant phase diagrams should be considered as an important step similar to performing a sensitivity analysis on the optimized parameters.

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Open Research

The software data used for geochemical modeling in the study are available at www.gwb.com via with license. The python code and model input scripts are available at <https://github.com/petermberger/minima> for free.

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