

A derivative method for analysis of surface potentiometric titration data and model optimization

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The pH buffering behavior of mineral and other natural surfaces is important to understanding the geochemistry and metal binding behavior of soils and sediments, and the stability and transport behavior of colloids. Hence, it is useful to investigate the proton buffering behavior of surfaces directly by potentiometric titration, and to develop predictive models. However, by most commonly used methods of data analysis, it is difficult to conduct a thorough qualitative comparison between model and observation in order to evaluate the appropriateness of the model. We have developed a derivative-based method for analysis of potentiometric titration data and optimization of surface protonation models that facilitates the qualitative examination of observation and model description. We implement this method in the computer program PROTOFIT.

The basis for the method is the calculation of a proton buffering derivative function that represents the proton buffering capacity of the surface as a function of pH as observed in the titration data. Thus, this function is ideal for comparing datasets obtained from different studies or under different experimental conditions. Furthermore, the proton buffering behavior sought from the titration is much more readily discernible from this function than from raw titration data. Also inherent to the method is an error estimate based on the smoothness of the proton buffering function; this estimate can be used to weight data points in the model optimization process.

The model optimization problem is approached by finding model parameters that provide a best fit between the observed proton buffering function and the model predicted function. Because no model assumptions are used in the calculation of the observed proton buffering function, virtually any surface complexation model can potentially be optimized by this approach (although PROTOFIT is currently programmed to optimize only a finite set of models). The method also allows for measured pH_{zpc} to be used as a constraint on the model optimization.

Observation of contact electrification between silicate melt/Pt and mineral/Pt phase interfaces

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Experimental Method

The experiment was performed in a one atmosphere experimental gas-mixing furnace utilizing a modified Pt suspension loop as an electrode with an additional Pt electrode through the center of the charge (Fig. 1). The experimental composition was a basaltic achondrite analog with spinel and/or olivine either at or very near the liquidus. The voltage between the two electrodes was monitored with a voltmeter board installed in a PC. The experiment was melted and equilibrated at QFM, 100 °C above the liquidus. With the temperature held constant at 1502 °C, still above the liquidus, the f_{O_2} of the furnace was changed from QFM to QFM +4.5 by turning off the CO gas. The voltage was allowed to stabilize and the f_{O_2} was reset to QFM.

Results

A plot of the voltage between the electrodes vs time (Fig. 2) reveals that increasing the f_{O_2} resulted in a positive voltage pulse of ~70 mV. between the electrodes and that the subsequent reduction of the f_{O_2} resulted in a negative voltage pulse of ~60 mV. between the electrodes. We attribute these voltages to changes in the work function of the melt due to the oxidation and reduction of Fe which resulted in differential contact electrification of the electrodes during the diffusion process. This experimental method can be used to perform real-time monitoring and analysis of the physical processes (*i.e.*, crystallization, melting, diffusion and changes in f_{O_2}) occurring during a petrologic experiment.

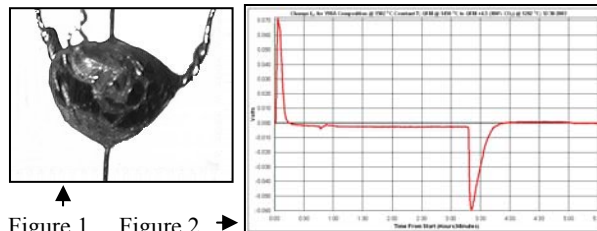


Figure 1. Figure 2. →

References

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