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Ken Overway
koverway@bridgewater.edu

John Oates
Bridgewater College

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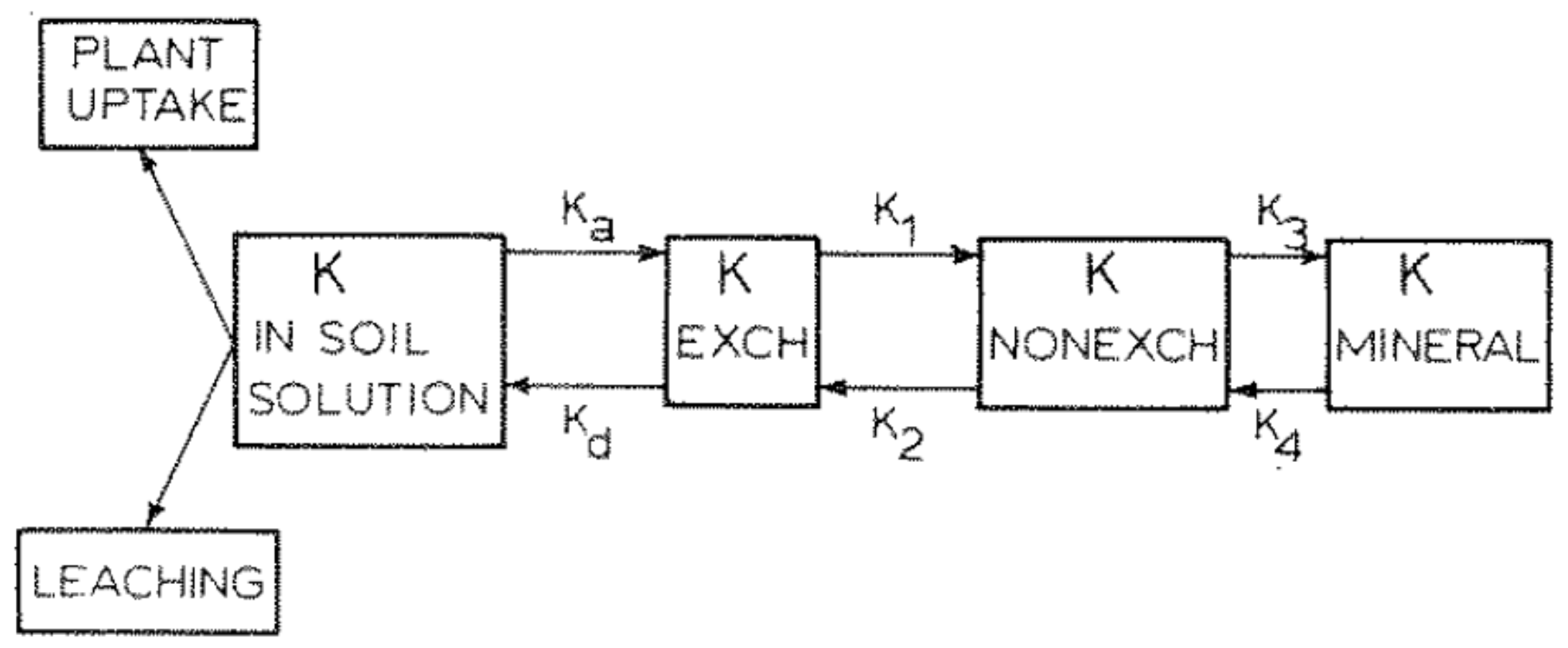
Acid Rain Kinetics on Calcareous and Silicate Soils

John T. Oates and Dr. Kenneth S. Overway

Department of Chemistry, Bridgewater College, 402 East College Street, Bridgewater, VA 22812-1599, USA

Introduction

Calcareous, silicate, and aluminosilicate minerals are common constituents of inorganic soil. These minerals act as buffers against acid attack, either through carbonate neutralization or cation exchange. Previous studies focusing on potassium observed that cations occur in four separate phases: the solution phase, exchangeable phase, non–exchangeable phase, and the mineral phase. Each phase represents a different kinetic mechanism that is incrementally slower for cations deposited deeper in the mineral.



We have observed that when soil is exposed to acid, the pH of the soil slurry drops drastically, followed by a recovery curve on the order of seconds to minutes. These recovery curves sometimes change curvature as a function of pH, indicating a different kinetic mechanism is dominating. Since real soil samples are a complex heterogeneous mixture, we analyzed soil analogs such as calcium carbonate, magnesium carbonate, calcium silicate, magnesium silicate, and aluminum silicate in the hope of assigning extracted kinetic parameters to specific physical properties of the compounds. We studied the kinetic mechanisms in these soil analogs with a series of hand titrations, designed to give a representation of the general shape of the reaction curve and the position of the equivalence point, and titration curves using an autotitrator, which was modified with a DAQ board in order to follow the recovery curve on a time scale of seconds between injections of acid. Our purpose was to determine the kinetic model for each type of recovery curve in each soil analog.

Experimental

Standardization of HCl

One liter of 1.0 M HCl was prepared by diluting concentrated HCl. A 1:10 dilution was made and this 0.1 M HCl was used to titrate Na_2CO_3 as a primary standard. The 1.0 M HCl was used for the autotitrator while the 0.1 M HCl was used for the hand titrations.

Hand Titrations

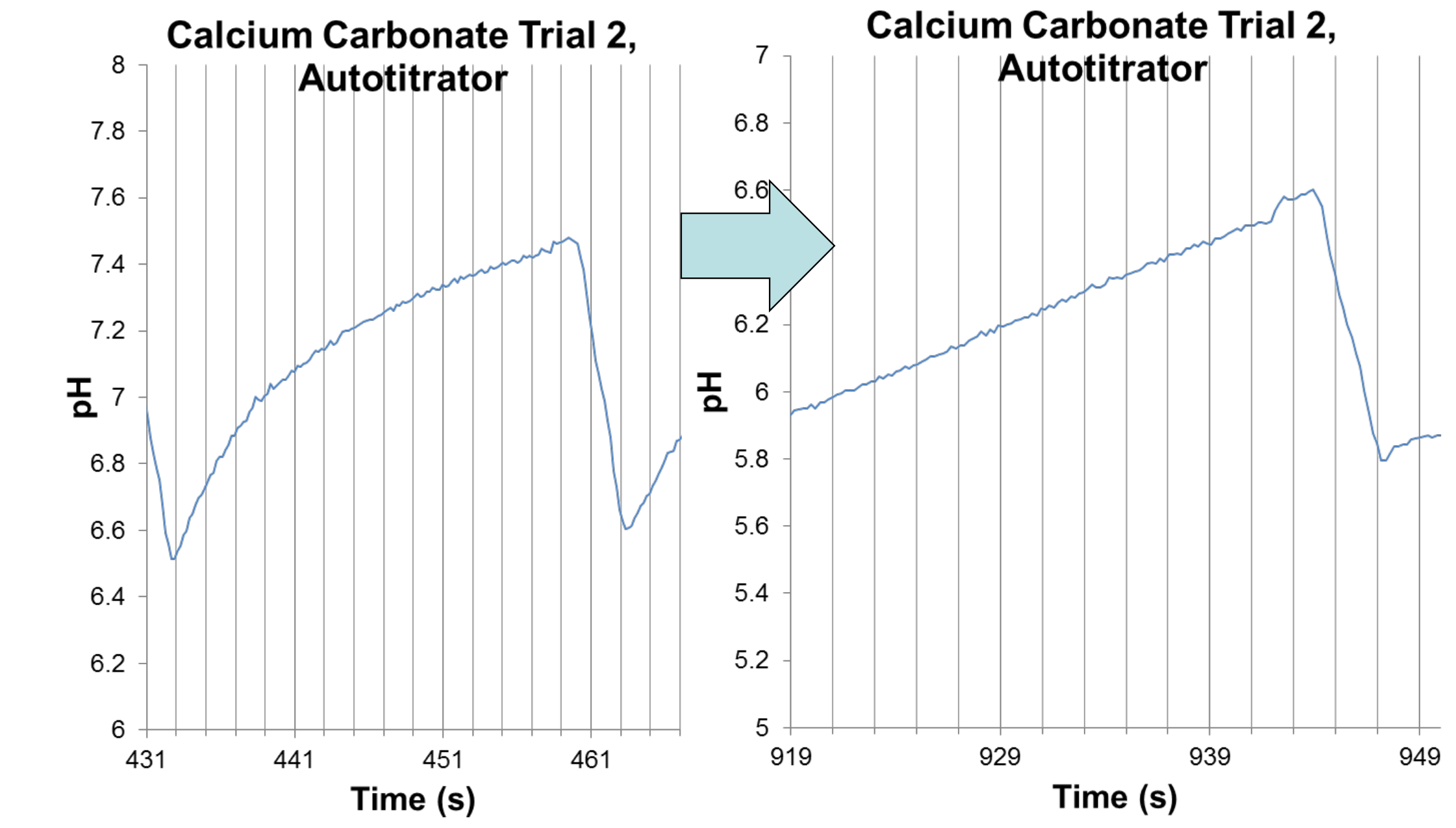
Samples of about 0.1 grams were placed into 150 mL beakers and filled with 50 mL of DI water. The sample was then titrated dropwise with standardized 0.1 M HCl. Each titration curve yielded an equivalence point.

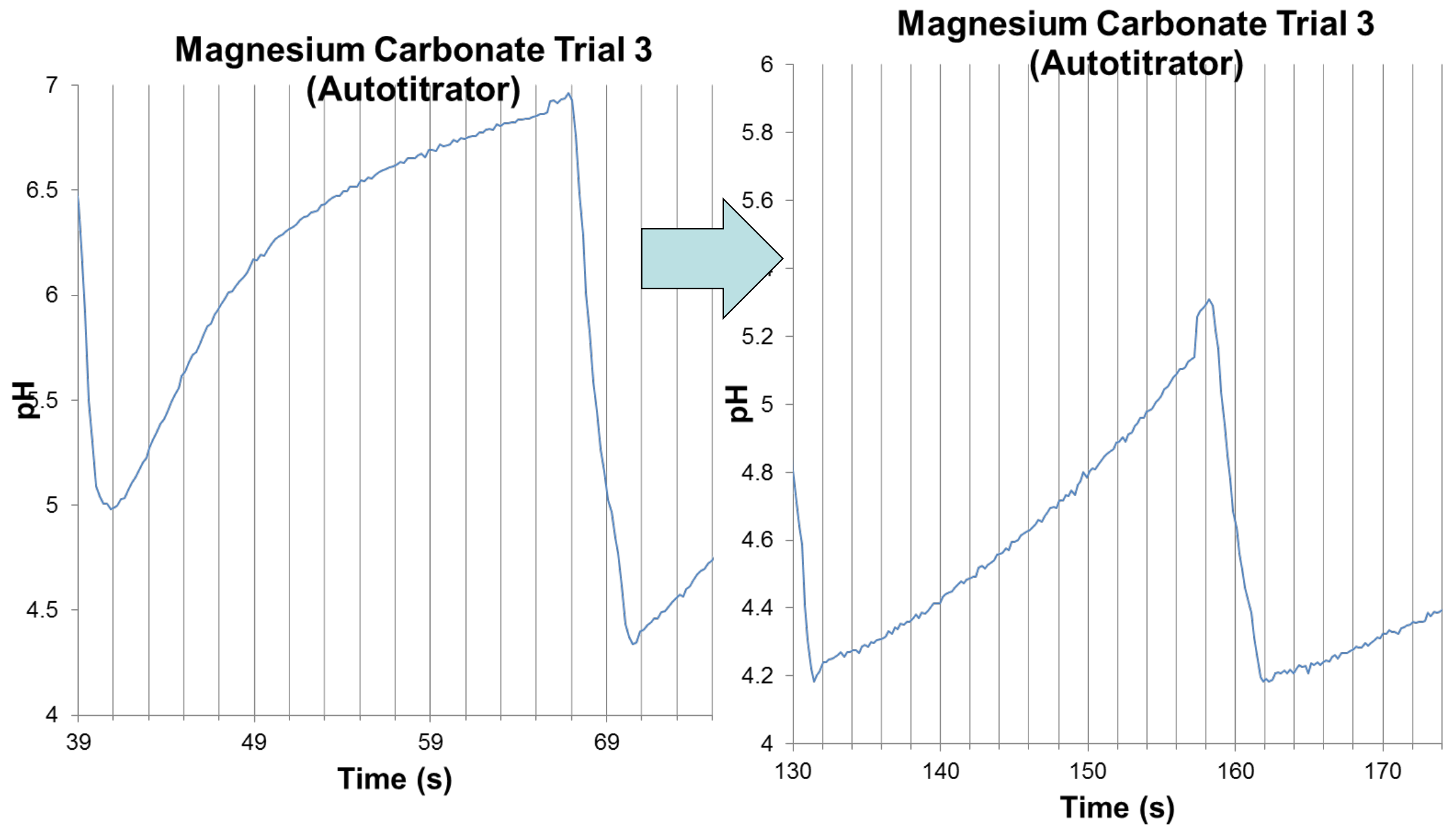
Autotitrator Stage

Samples of about 0.1 grams were placed into 150 mL beakers and filled with 60 mL of DI water. A Metrohm 736 Titrino autotitrator was programmed to inject 1.0 M acid in microliter aliquots. Variable delays between aliquots allowed the collect of the recovery curves seen below. Parameters included: injection volume, equilibration time, and the ending pH.

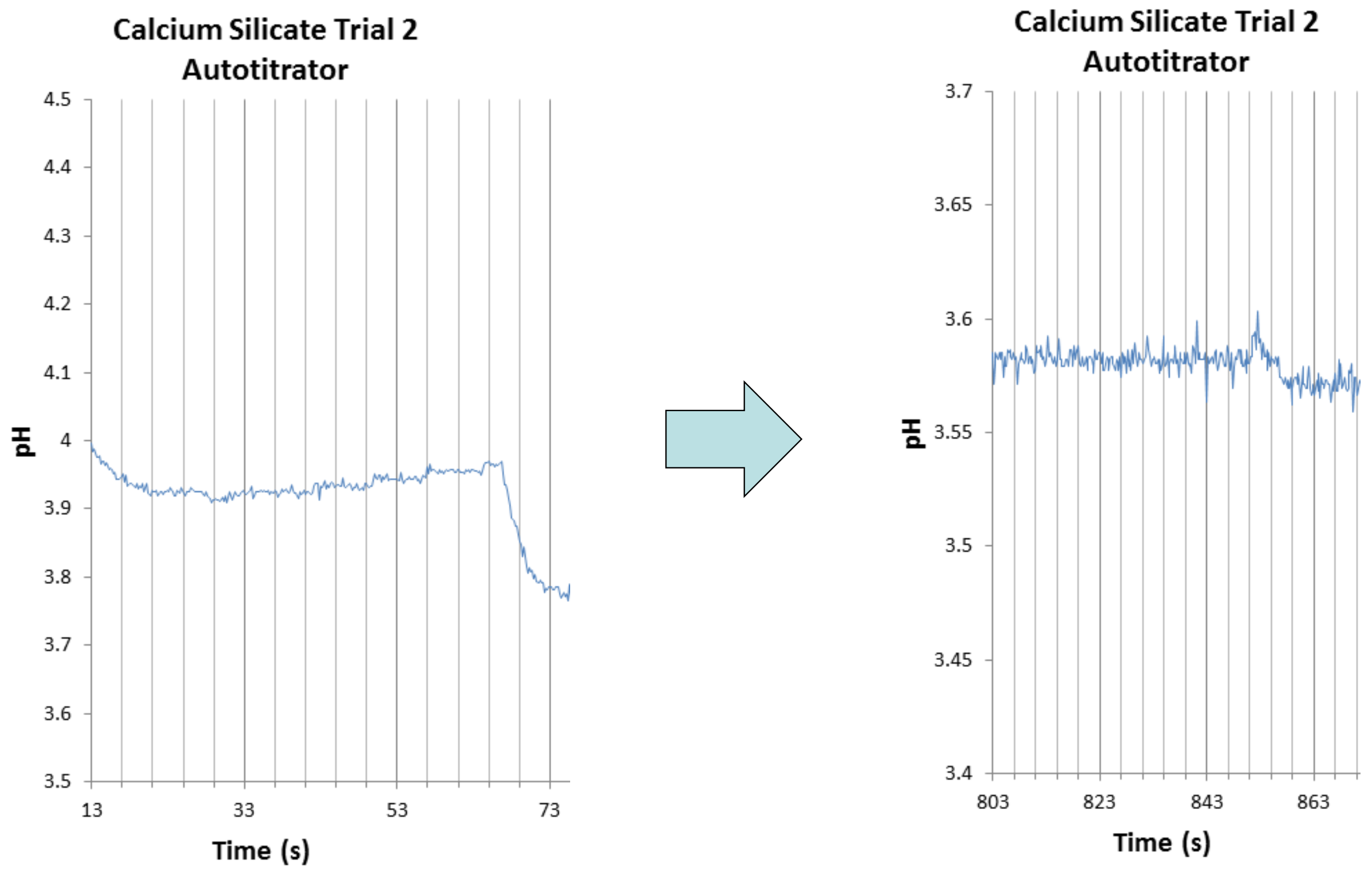
Results

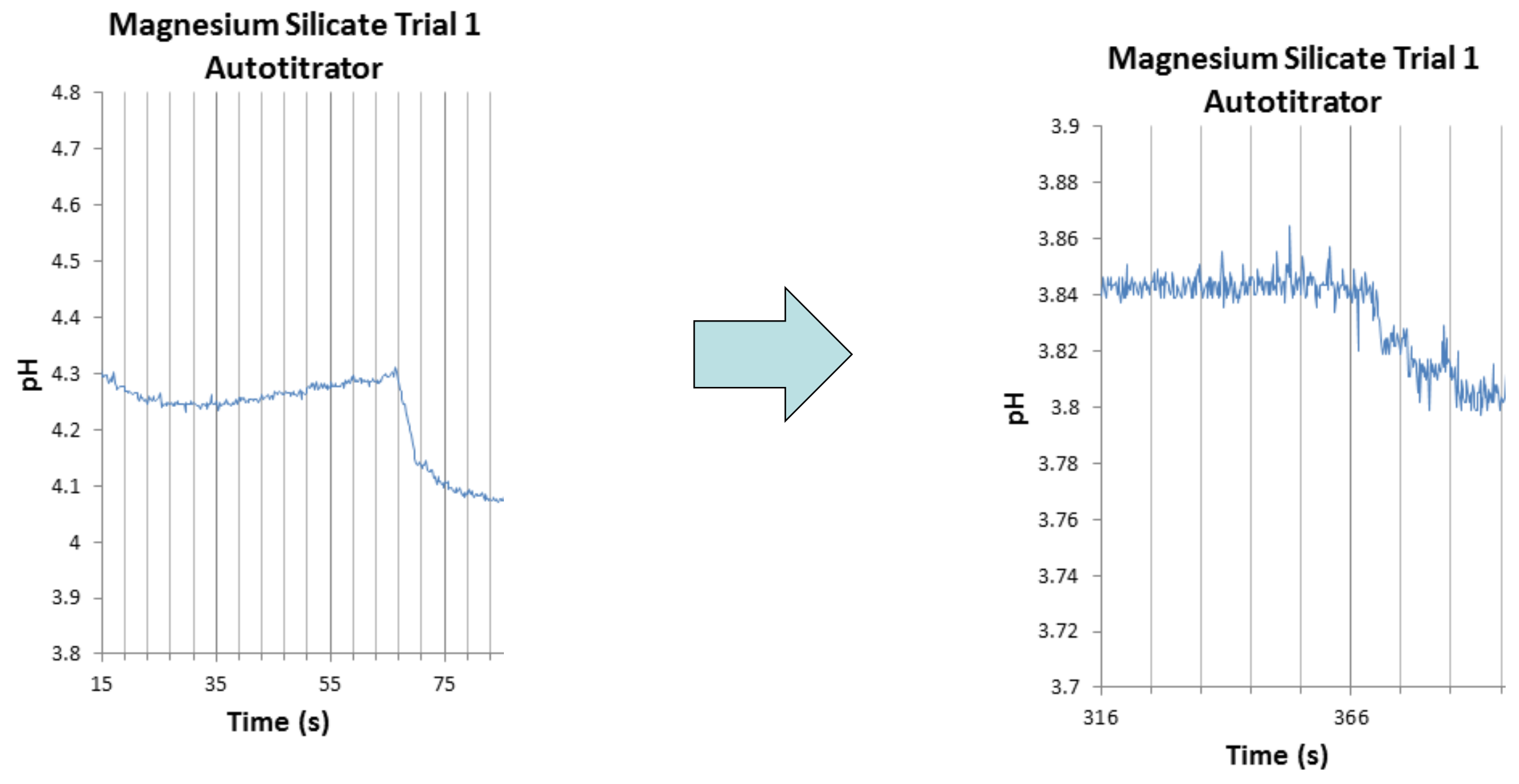
Recovery curves from carbonate samples show a distinct change in the reaction mechanism.





Recovery curves from the silicate minerals are much weaker and do not show a significant change in the reaction mechanism, just an attenuation of the recovery.



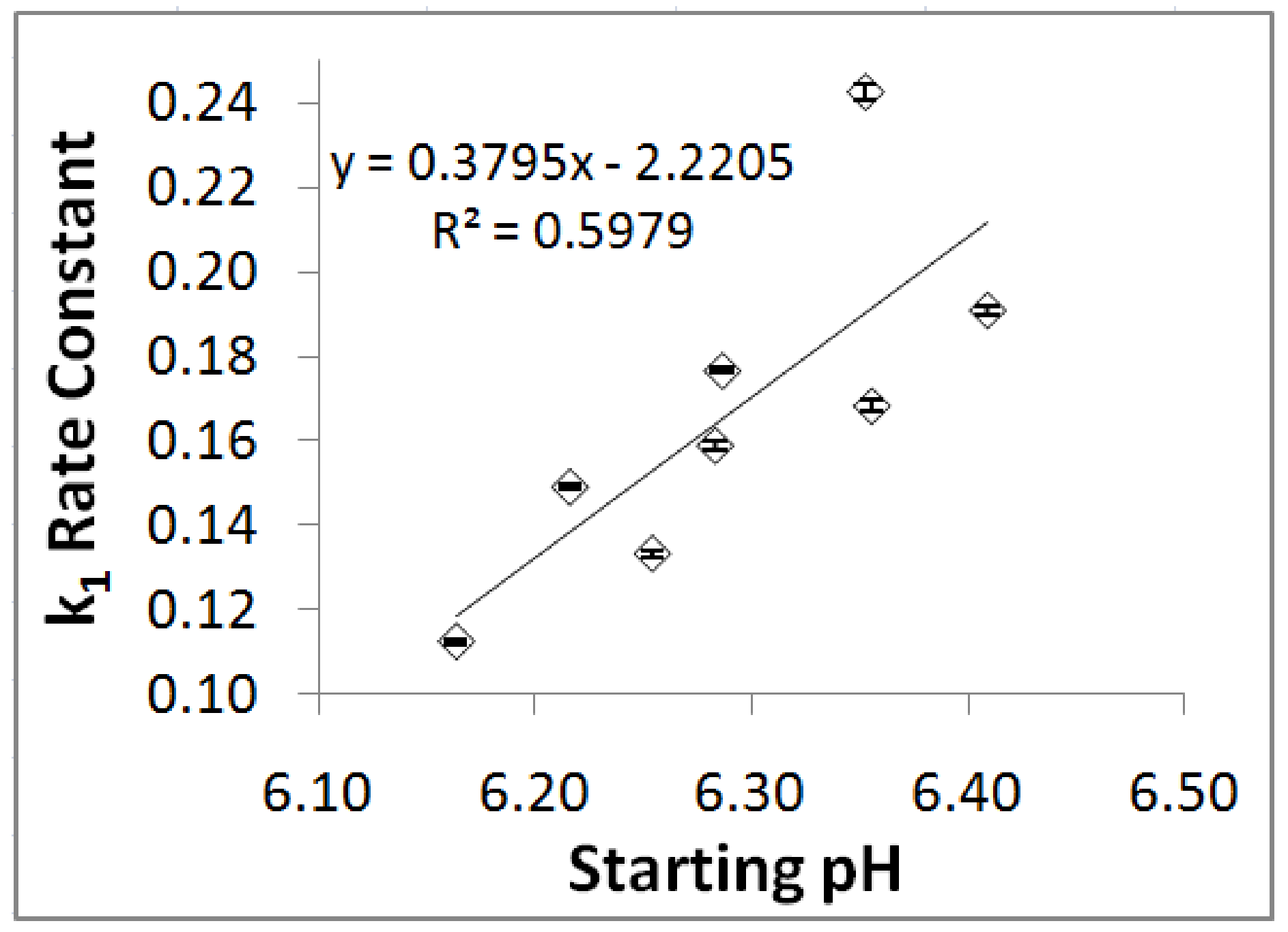


Previous work suggested that the kinetics involved reversible processes, so several recovery curves of $CaCO_3$ were fit to a 1st order reversible model represented by the following equation.

$$H^+(aq) + soil - M(s) \underset{k_2}{\overset{k_1}{\rightleftarrows}} soil - H + M^+(aq) \quad [H^+] = \frac{[H^+]_0 e^{(-(k_1+k_2)(t-t_0))} + \frac{k_2}{k_1}}{1 + \frac{k_2}{k_1}}$$

where $[H^+]_0$ is the hydronium ion concentration at the beginning of the recovery curve, t and t_0 represent the time, and k_1 and k_2 are the rate constants. When this model was applied to the recovery curves from pH 6.1-6.4 region the following rate constants were extracted using nonlinear regression analysis.

Start pH	k_1	k_2
6.35	0.2425 ± 0.0021	0.03731 ± 0.00092
6.41	0.1911 ± 0.0011	0.03024 ± 0.00053
6.36	0.1684 ± 0.0015	0.02143 ± 0.00070
6.29	0.17670 ± 0.00069	0.02234 ± 0.00033
6.28	0.15895 ± 0.00098	0.02051 ± 0.00056
6.22	0.14911 ± 0.00068	0.01708 ± 0.00039
6.25	0.13329 ± 0.00061	0.01890 ± 0.00048
6.16	0.11242 ± 0.00052	0.01070 ± 0.00043



Discussion

Clearly there is a strong correlation between the pH and the rate constants, with the graphical relationship for k_1 show below. More work needs to be done on the relationship between the adsorption of hydronium and the changing rate as a function of pH.

Acknowledgements & References

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