Towards The Development of Rare Event Simulation Methods For Improved Mechanistic Understanding of Mineral Surface Reactivity

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The mechanisms of mineral dissolution and growth are often viewed through the lens of water exchange kinetics. This is with good reason, as well-established reactivity trends indicate a high degree of correlation between the kinetics of mineral dissolution and the rates of water exchange about their constituent ions in solution. However, dissimilarities between interfacial and solution-borne reactions are also recognized. Namely, water exchange reactions are elementary processes consisting of a single reaction step in which one coordinating ligand is replaced by an equivalent ligand, whereas ion detachment and attachment reactions are known to be complex chain reactions that involve the dissociation of multiple bonds and the exchange of both surface and solvent associated ligands. Although solvent dynamics at the mineral-water interface clearly influences reactivity, the mechanistic differences between reactions that lead to water exchange and those that lead to ion attachment and detachment remain unrecognized. Molecular scale simulations have gained prominence in investigations of interfacial solvent structure and dynamics. However, due to intrinsic limitations, it is generally impossible to reach the length and timescales needed to simulate ion attachment or detachment without employing specialized simulation methods designed to enhance the rate at which rare events are sampled. Most methods in this class achieve success by imposing a bias in the simulation that accelerate exploration along certain degrees of freedom or “collective variables” deemed important to drive the reaction of interest to completion. Rarer, are path sampling methods that aim to discover reaction pathways without imposing a bias.

The overarching goal of this project is to develop new simulation tools that can be used to quantify the rates and mechanisms of complex multistep reactions at the mineral-water interface. Our methodology is based on the established forward flux sampling approach (FFS), which allows for the rates of rare events to be calculated without applying a bias to the simulation and without specifying an initial reactive pathway. Our efforts build upon the significant body of previous literature devoted to the study of rare events and is driven by the underlying hypothesis that reaction progress can be described using time as a transition parameter, rather than a geometrically defined order parameter or reaction coordinate. Further, we anticipate that using time as a transition parameter in FFS simulations will: **(1)** reduce or eliminate sampling bias; **(2)** facilitate the identification of competing reaction channels; and **(3)** enable unbiased searches for important metastable states.

In principle, using time as a reaction progress coordinate enables us to both identify multiple and/or competing reaction pathways and to perform unguided and unbiased searches for important intermediate states along complex reaction pathways. As this is an ambitious long-term goal, our efforts have focused on ligand exchange reactions in solution and at the mineral-water interface that are reasonably constrained by prior experimental and theoretical observations. To reach these ends, four main project objectives are outlined in the original application. These are: **(1)** implementation of FFS with time as a reaction progress coordinate; **(2)** understand influence of solution conditions on ligand exchange pathways; **(3)** compare solution-borne and interfacial ligand exchange reactions; and **(4)** produce open-source software tools. Although it was not a stated as an explicit goal in our original application, our long-term interest in oxide/silicate mineral reactivity requires us to rely on reactive forcefields. Therefore, we have also evaluated the ability of several reactive models to accurately simulate Si-O bond hydrolysis in solution.

These objectives are consistent with cross-cutting challenges outlined in several recent Office of Science and Office of Basic Energy Sciences workshop reports in the areas of geoscience[1,2] and environmental management[3], computational materials science at the nano- and mesoscales[4–6], catalysis[7], and the control of matter far from equilibrium[8].

Research Accomplishments

Objective 1: Implement modified FFS algorithms

Our implementation of FFS using time as a transition parameter is based on the "direct" FFS algorithm[9]. This approach is computationally efficient but requires a large number of configurations to be stored. In our initial application we indicated that we would consider using the "branched growth" or "Rosenbluth-like" FFS algorithms[10,11] as they generate reactive trajectories sequentially rather than in parallel which this makes the extraction of successful trajectories simpler and greatly reduces the number of trajectory segments and configurations that need to be stored during the calculation. In the end we determined that the direct algorithm was suitable for our purposes, and that it was not worth the effort to completely reengineer our workflow. Our code consists of two python scripts that control the execution of the LAMMPS simulation engine. Our implementation also makes use of internal features within LAMMPS; notably the built in "jump" command, which can be used to define blocks of commands within the input file that are executed conditionally. These input blocks are employed in our code to detect when a trajectory has entered the product state or returned to the reactant basin, to count the number of timesteps a given trajectory remains outside of the reactant basin, to save configurations and write trajectory files, and to clean up failed trajectories. A number of other python utility scripts have also been generated to assist in the final determination of rate constants and to stitch together trajectory segments into complete reactive trajectories.

Objective 2: Understand influence of solution conditions on ligand exchange pathways

Our initial studies focused on comparing the performance of our FFS method against the findings of established methods for quantifying the kinetics of ligand exchange about ions in solution. In these studies, we focused on modeling the exchange of water molecules within the first hydration shell of metal aquo ions (M^{Z}). Conventionally, this process is described as follows:

$$[\mathrm{M}^{Z}(\mathrm{H_2O})_{n}] + \mathrm{H_2O}^{*} \overset{k_{ex}}{\longleftrightarrow} [\mathrm{M}^{Z}(\mathrm{H_2O})_{(n-1)}\mathrm{H_2O}^{*}] + \mathrm{H_2O} \tag{1}$$

where *Z* is the valance state of the metal, *n* is the number of exchangeable molecules contained within the hydration shell, k_{ex} is the reaction rate constant, and * denotes the identity of the substituent water molecule in the surrounding solution.

We set out to demonstrate that our novel FFS approach produces rate constants that are statistically equivalent to direct simulations methods used to obtain water exchange rates about fast exchanging ions in solution. For this purpose, we calculated the rate of water exchange about Li^{+} and Ca^{2+} by three methods: (1) direct counting; (2) integration of the residence time correlation function; and (3) FFS with time as a reaction progress coordinate. Upon comparing the results of the direct simulation methods (i.e., direct counting and analysis of the residence time correlation function) with FFS, we came across an unexpected and long-standing inconsistency in the literature. That is, the rate constant for water exchange (k_{ex}) is conventionally defined with respect to the lifetime or residence time of a water molecule within the first hydration shell as follows:

$$k_{ex} = \frac{1}{\tau_{res}} \tag{2}$$

However, our simulation results demonstrate that the residence time is not strictly equivalent to the reaction period (τ_{rxn}) when multiple ligands are exchangeable. Futher, our findings show that the exchange rate constant (k_{ex}) deviates from that of the elementary processes (k_{rxn}) in a predictable fashion as the number of labile ligands in the solvation shell increases according to the following relationship:

$$k_{rxn} = nk_{ex} = \frac{1}{\tau_{rxn}} \tag{3}$$

The relationship between k_{ex}, k_{rxn}, and n illuminated above has been tacitly alluded to in some previous work, but the physical distinction between k_{rxn} and k_{ex}, and the impact of this relationship on $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$, was not explored by earlier studies. Because k_{ex} scales with the frequency of every n^{th} exchange reaction, or the turnover rate of the solvation shell, it accounts for only a fraction $(1/n)$ of the total number of activated complexes that form and successfully decompose to products per unit time. However, k_{rxn} always scales in exact parity with the exchange frequency, irrespective of the number of labile ligands in the coordination shell. Consequently, Eyring-type kinetic analyses that rely on k_{ex} rather than k_{rxn} do not consider the full statistical weight of the activated complex and underreport the entropic component of the activation free energy. Consequently, when activation parameters (i.e., $\Delta G^{\ddagger}, \Delta H^{\ddagger}, \Delta S^{\ddagger}$) are determined by performing and Eyring analysis with respect to k_{ex} rather than k_{rxn}, we erroneously arrive at a negative activation entropy, which in turn results in a significant overestimate in the value of $\Delta G^{\ddagger}$. This work formed the foundation of a student's master's thesis. We submitted a version of the manuscript on this topic to *Nature Communications*. We are currently revising this manuscript for another journal (Wallace et al., *in prep*).

While this was a successful test of our methodology, we also needed to ensure that our approach would remain effective for reactions whose rate constants cannot be determined by direct simulation methods. For this purpose, we shifted focus to apply our FFS method to the magnesium ion. Our initial efforts to do so were plagued with failures. After tremendous effort we decided to perform a survey of available magnesium-water interaction potentials in the literature to determine which if any available models were capable of approximating experimental exchange rates. Our survey made use of 500 nanosecond long direct simulations performed at 373K. Under these conditions, we found that most of the models surveyed that utilized a standard 12-6 Lennard-Jones potential dramatically underestimated the exchange rate by several orders of magnitude. In fact, for several popular potentials, no exchanges were observed during our direct simulations at all. However, we did identify a handful of interaction potentials that utilized either the TIP4P water model and/or the 12-6-4 form of the Lennard-Jones potential that exhibited exchange rates comparable to experiment. We selected two well-performing interaction potential models from our high temperature direct simulations that utilized the 12-6-4 form of the Lennard-Jones potential to conduct additional reactive flux and

FFS rate calculations at 373K and 298K. Our results show that within the uncertainties, both the reactive flux and FFS derived rates agree with the rates obtained from our direct simulations. Further, agreement was achieved between the reactive flux and FFS rates at 298K, where rates cannot be obtained by direct simulation (Ma et al., *in prep*). This result is important, because it demonstrates the statistical equivalence of our FFS derived rates with those obtained from established and widely employed rare event theories (i.e., reactive flux).

Objective 3: Compare solution-borne and interfacial ligand exchange reactions

Although simple oxides[12,13], orthosilicates[12,14], and rhombohedral carbonates[15] exhibit reactivity trends that are highly correlated with solution-borne ligand exchange reactions[16], the mechanistic aspects of these reactions are not necessarily similar. To investigate these differences, we originally proposed to extend our efforts to understand the influence of solution conditions on reaction pathways to the mineral water-interface, specifically, we proposed to focus on the kinetics of ion attachment and detachment at the calcite-water interface.

In our FFS rate calculations of water exchange about ions in solution we were able to determine whether a given simulation trajectory had reached the product state by monitoring the change in water coordination number over time. If a water molecule originally in the first hydration shell moved to the second, the coordination number, calculated only over the molecules initially within the first shell, would decrease by a value of 1. By comparison, monitoring the progress of an ion attachment / detachment reaction from the mineral water interface is much more challenging, as multiple locally stable states are possible. Moreover, as mineral surfaces may exhibit multiple types of reactive sites, we would expect the topology of the free energy landscape to vary from site-to-site.

For the reasons stated above, we decided to focus on a single surface site (an obtuse kink site on the (104) surface of calcite), and to monitor the reaction progress as a function of 2 coordination numbers. The first coordination number tracked the number of water molecules located within the ion's first hydration shell, while the second coordination number tracked the number of bonds connecting the ion to the mineral surface. To obtain an understanding of where all the locally stable states were located, we used the well-tempered metadynamics method to map out the free energy landscape for ion detachment / attachment with respect to both coordination numbers. The resulting energy landscapes revealed the presence of multiple free energy minima between the attached and detached states. It took us quite a while, but once we knew where the energy minima were located on the free energy landscape, we were able to devise an order parameter to determine where a given simulation trajectory was located on the landscape. With this capability, we were able to use our FFS approach to calculate the fluxes to and from each free energy basin on the landscape.

The equilibrium constants for each step of the ion attachment / detachment chain reactions were derived from the FFS derived reaction rates. In turn, these equilibrium constants were combined to derive an effective solubility product for the obtuse kink site ($K = 10^{-7.46}$) which is of the same order as the bulk solubility product calculated for the same potential model by free energy perturbation ($K_{sp} = 10^{-7.9}$) [17].

The similarity of the site specific and bulk solubility products gave us confidence in the fidelity of the reaction trajectories that we harvested between each of the free energy minima. Upon consideration of the reaction rates for ion attachment and detachment, we concluded that the rate of calcium detachment is rate limiting for dissolution at this site (i.e., the Ca^{2+} transition from 3-to-2 surface ligands is the slowest step for detachment), whereas carbonate ion attachment is rate limiting for growth (i.e., the CO_3^{2-} transition from 2-to-3 surface ligands is the slowest step for attachment). We were able to obtain further insights into the mechanisms of these rate limiting steps by analyzing large numbers (>2000) of reactive trajectories. From this analysis we determined that the over-coordination of Ca^{2+} by water drives both the water exchange and ion detachment processes. At equilibrium, Ca^{2+} is bound to three water molecules in the obtuse kink. During water exchange, the kink site calcium briefly takes on a fourth water molecule before returning to its equilibrium configuration. However, two water molecules are adsorbed at the onset of calcium detachment. Carbonate ion attachment is also controlled by adsorbed water at the kink site which prevents the ion from establishing 3 bonds to the surface. Carbonate attachment occurs at the kink when the surface bound water diffuses out of the kink site. These findings will be presented in a forthcoming Ph.D. dissertation and are being prepared for submission to *ACS Earth & Space Chemistry* (Schmidt et al., *in prep*).

Objective 4: Produce open source software tools

As we are still working on the preparation of several publications, we have not yet made our code publicly available. However, we have created a Github repository (https://github.com/afwallace/PYTHON_FFS) in which we are preparing to release our code with documentation and examples under the GNU General Public License by September 2025. We also plan to use the Cern hosted Zenodo repository to obtain a DOI for our Github repository.

Objective 5: Assessment of Reactive Potentials for Si-O Bond Hydrolysis

In this study we assessed the ability of several empirical reactive potentials to describe the energetics of Si – O bond hydrolysis. DFT studies have shown that the Si-O bond hydrolysis can be driven by nucleophilic attack of silicon by water, which proceeds at neutral conditions through the formation of a pentacoordinate intermediate state in which the bridging oxygen site

(O_{br}) accepts a proton from the adsorbing water molecule. Therefore, the Si-O_W distance (O_W = oxygen atom in a water molecule) might be considered an adequate description of the hydrolysis reaction progress coordinate. However, because prior investigations have treated solvent in a very limited way (i.e. through the inclusion of a single water molecule in the gas phase), questions remain as to the most likely protonation mechanism for the bridging oxygen. As one aim of this study was to investigate bond hydrolysis in a fully solvated environment, a more flexible description of the reaction progress coordinate was used that prescribes as little about the reaction mechanism as possible.

Our simulations utilized a reaction progress coordinate that is composed of two collective variables (CV). CV_1 is the minimum distance between any silicon atom and any water-associated oxygen atom in the simulation. CV_2 is defined as the maximum length of and Si-O bond to the bridging oxygen. The overall reaction progress coordinate is defined as $\xi = CV_1 - CV_2$.

$$\xi = \mathrm{CV}_1 - \mathrm{CV}_2 = \mathrm{MIN}(Si - O_W) - \mathrm{MAX}(Si - O_{br}) \qquad (4)$$

This definition ensured that identity of the nucleophilic water molecule was not prescribed. Moreover, as the positions of protons are not considered in the definition, no assumptions were made regarding the protonation of the bridging oxygen site.

Classical well-tempered metadynamics simulations were performed with this reaction progress coordinate to obtain free energy landscapes for Si-O hydrolysis for three ReaxFF potentials [18–20] and a Stillinger-Weber type potential at 25°C [21,22]. Our simulation results revealed that at long run times, all three ReaxFF style potentials produce energy landscapes in which the 5-coordinated state is over-stabilized. As a result, the energy landscapes for these models exhibit a local minimum for the 5-coordinated state. In contrast, Garofalini's Stillinger-Weber style potential produced well-converged free energy landscapes for Si-O hydrolysis and correctly described the 5-coordinated state as a transition state. Additionally, when analyzing energetic data, the Garofalini model performs the best quantitatively, having also succeeded in reasonably reproducing the experimental free energy of reaction and activation free energy within the range predicted by DFT calculations. The Garofalini potential is recommended for future simulation studies on this basis (Schmidt et al., *in prep*).

Collaborations with DOE Researchers

Prior to the COVID-19 pandemic we planned to host a Stephan Irle and Nikhil Rampal (Oak Ridge National Laboratory) at the University of Delaware, however, these plans were paused indefinitely. We have collaborated with fellow Geoscience program PI Ian Bourg, and other DOE lab scientists (Jim De Yoreo, Jinhui Tao, PNNL) on a study to quantify the influence of curvature on the hydrophobicity of clay mineral surfaces (Fernandez-Martinez et al., 2020).

DOE Sponsored Research Products

Project results have been disseminated through presentations at academic institutions and at conferences sponsored by major scientific societies (i.e., American Chemical Society, Geochemical Society, Geological Society of America, Society of Engineering Sciences). Results have also been published in two master's theses. One forthcoming doctoral dissertation is expected in Summer 2024. The manuscripts that form the chapters of the doctoral dissertation are required to be submitted for publication prior to approval of the dissertation by the Department. A Github repository has been setup to host our FFS codes and documentation and to make the tools we have developed freely available. Our code is not yet available as we are still in the process of publishing our findings. We are continuing to advance the studies described above towards publication.

Theses and Dissertations

Schmidt, T.D., Applications of Forward Flux Sampling with Time as a Reaction Progress Coordinate, expected completion date Summer 2024.

Hazewski, June A., Modeling Si-O Bond Hydrolysis with Reactive Potentials. University of Delaware ProQuest Dissertations & Theses, 2020. 27999070. https://www.proquest.com/pqdtlocal1006271/dissertations-theses/modeling-si-o-bond-hydrolysis-with-reactive/docview/2702131241/sem-2?accountid=10457

Ma, Yifei, The Kinetics of Water Exchange and the Entropy of Activation Revisited. University of Delaware ProQuest Dissertations & Theses, 2019. 13864133. https://www.proquest.com/pqdtlocal1006271/dissertations-theses/kinetics-water-exchange-entropy-activation/docview/2700869359/sem-2?accountid=10457

Accepted Publications

Fernández-Martínez, A., Tao, J., Wallace, A.F., Bourg, I.C., Johnson, M.R., De Yoreo, J.J., Sposito, G., Cuello, G.J., and Charlet, L., Curvature-induced hydrophobicity at imogolite-water interfaces, Environmental Science: Nano, 2020, 7 (9), 2759-2772

Publications in Preparation

Wallace, A.F., Schmidt, T.D., and Ma, Y., The Kinetics of Water Exchange and the Entropy of Activation Revisited. In prep for *J. Phys. Chem.*

Ma, Y., and Wallace, A.F., Rare event simulations of water exchange on Mg^{2+} using standard biomolecular force fields. In Prep for *J. Chem. Theory Comput.*

Schmidt, T.D., Quadery, A., and Wallace, A.F., Rate Determining Processes at the Calcite-Water Interface. In prop for *ACS Earth Space Chem.*

Schmidt, T.D., Hazewski, J., and Wallace, A.F., A Critical Survey of Reactive Potentials for Si-O Bond Hydrolysis. In prep for *Chemical Geology*

Invited Lectures

1) Wallace A.F. and Schimdt, T.D., Department of Civil and Architectural Engineering, University of Miami, 2024.

2) Wallace A.F. and Schmidt, T.D., Reassessment of the Roles of Ion Hydration and Dehydration on the Reactivity of the Calcite-Water Interface, Geological Society of Washington D.C., 2024.

3) Wallace A.F., Towards and improved understanding of mineral surface reactivity: Current practices and future opportunities in computational geochemistry. Princeton University, Department of Geosciences, 2018.

Invited Conference Abstracts / Presentations

4) Wallace A.F., Quadery, A., and Schmidt, T., Simulated detachment of ions from calcite (104): Insights from metadynamics and forward flux sampling. American Chemical Society Spring Meeting, Philadelphia, PA, 2020. Meeting Cancelled Due to COVID-19

5) Wallace A.F. and Quadery, A., Towards improved simulation methods for mineral surface reactivity. Society of Engineering Sciences, Washington University, St. Louis, MO, 2019. Oral Presentation

6) Wallace A.F., and Ma, Y., Application of a novel forward flux sampling procedure to the kinetics of water exchange on Li^{+}, Ca^{2+} and Mg^{2+}. American Chemical Society Fall Meeting, Boston, MA, 2018. Oral Presentation

7) Wallace A.F., A forward flux sampling method for probing geochemical reaction rates and mechanisms with molecular dynamics simulations. V.M. Goldschmidt Conference, Boston, MA, 2018. Oral Presentation

Contributed Conference Abstracts / Presentations

8) Schmidt, T.D. and Wallace, A.F., Kinetics Ligand-Exchange Mechanisms and Solvation Dynamics Related to Ion Attachment and Detachment at the Calcite-Water Interface. V.M. Goldschmidt Conference, Chicago, Illinois, 2024. Oral Presentation

9) Schmidt, T.D. and Wallace, A.F., Kinetics of Water Exchange and Ion Detachment at Obtuse Kink Sites on Calcite (104). V.M. Goldschmidt Conference, Lyon, France, 2023. Oral Presentation

10) Schmidt, T.D., Wallace, A.F., Quadery A.H., Kinetics of Water Exchange and Calcium Detachment at the Calcite-Water Interface. American Chemical Society Spring Meeting, San Diego, CA, 2022. Oral Presentation

11) Schmidt, T.D., Wallace, A.F., and Quadery, A.H., Metadynamics Simulations of Ion Detachment from Calcite (104). American Chemical Society Spring Meeting, San Antonio, TX, 2021. Oral Presentation

12) Quadery, A. and Wallace, A.F., Assessing the influence of spectator ions on the kinetics and mechanisms of ligand exchange at the calcite (104)-water interface. Geological Society of America Annual Meeting, Phoenix, AZ, 2019. Oral Presentation

13) Hazewski, J. and Wallace, A.F., Modeling Si-O bond hydrolysis with ReaxFF potential models. Geological Society of America Annual Meeting, Phoenix, AZ, 2019. Oral Presentation

14) Ma, Y. and Wallace, A.F., Water Exchange rates and reaction pathways on Mg^{2+}. V.M. Goldschmidt Conference, Boston, MA, 2018. Poster Presentation

15) Hazewski, J. and Wallace, A.F., Metadynamics simulations of Si-O bond hydrolysis using ReaxFF potential models. V.M. Goldschmidt Conference, Boston, MA, 2018. Poster Presentation

Other Presentations

16) Schmidt, T.D., Kinetics of water exchange and ion detachment at obtuse kink sites on calcite (104). Delaware Environmental Institute Research Symposium, 2023. Poster Presentation

17) Wallace A.F., Applications of high-performance computing in geochemistry. University of Delaware High-Performance Computing Symposium, 2018. Oral Presentation

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