

# **A forward flux sampling method for probing geochemical reaction rates and mechanisms with molecular dynamics simulations**

A.F. WALLACE<sup>1</sup>

<sup>1</sup>Department of Geological Sciences, University of Delaware, Newark, DE 19716, USA (\*correspondence: afw@udel.edu)

An understanding of the interactions between fluids and geological materials in subsurface environments is required to address ongoing and future energy related challenges. These include: mitigation of organic and inorganic contaminants associated with mining operations, hydraulically fractured oil shales, and nuclear materials; evaluation of potential sites for long-term storage of atmospheric carbon dioxide and spent nuclear waste; and utilization of carbon dioxide for enhanced oil recovery. The inherent challenges involved in accessing the subsurface necessitates the use of theoretical models to investigate subsurface processes. In this regard, molecular scale simulations are particularly valuable tools because they provide mechanistic insights into chemical processes that are difficult to discern from macroscale observations. However, at present the applicability of molecular scale simulations is generally limited to short time and length scales. Therefore, there is a critical need to develop simulation methods that can circumvent these timescale limitations and provide mechanistic insights into reactive events using existing high-performance computing resources.

The forward flux sampling (FFS) method is an efficient computational procedure for calculating the rates of rare events from molecular dynamics simulations. The rate is calculated as the product of the reaction attempt frequency with the probability of reaching the product state from the reactant state. This probability is generally too small to be calculated directly, and is itself obtained as the product of several larger probabilities associated with reaching certain milestones en route to the product state. In existing implementations of the FFS method, these milestones are defined in terms of one or more user specified collective variables (CV), and the definition of the CV can have a significant influence on the calculated rates and reaction mechanisms. Herein, we present progress on the development of a custom FFS procedure that may overcome these limitations, and demonstrate the method's potential utility in investigations of dynamic processes at the mineral-water interface.