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The problematic use of Transition State Theory in mineral dissolution

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For decades Transition State Theory (TST) and TST-based rate laws have been utilized as the major theoretical approach to describe and quantify mineral and glass dissolution kinetics. However, despite concerns raised in an increasing number of reports published over the past decade over the applicability of TST to overall mineral dissolution kinetics, geochemistry and related disciplines involved in e.g., cement hydration and nuclear waste management engineering, have continuously utilized this tool.

There is now mounting evidence from experimental studies, molecular scale simulations, and fundamental theoretical work detailing the problems that arise when TST is applied to the dissolution of minerals and crystalline materials in terms of the relationship between dissolution rate and free energy, ΔG. For a large number of crystalline and glass phases, there is critical disagreement between experimentally-observed versus TST-predicted rates, particularly in the region of Gibbs free energy between macroscopic equilibrium and the so-called dissolution plateau. This disagreement exists for both complex phases such as framework silicates as well as simple carbonates. This fact should generate concern: first, within the scientific community over the correctness of our basic scientific approach, and secondly on the part of decision makers over the consequences that society bears as a result. Indeed, the result may be that we are collectively unaware of the greater risk we are assuming by using flawed TST-based model predictions.

A possible solution may lie in tackling mineral dissolution as a stochastic problem. This approach focuses on the probabilistic aspects of the dissolution process, and abandons the assumption that *crystal dissolution can be adequately characterized by a unique rate constant*. In taking this new path, we would have to recognize that variations in dissolution rate “constants” may not always reflect extrinsic factors, but instead reveal controls intrinsic to the mineral itself.