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Editorial

George W. Luther III[1]

Dear Readers

Starting with Victor M. Goldschmidt in the early part of the twentieth century, geochemists have used thermodynamics to understand aquatic and geochemical processes. In the last four decades, geochemists have increasingly used chemical kinetics to understand the rates of geochemical reactions, which further permit prediction of these processes in the environment over large scales. However, the use of chemical kinetics is normally considered a less straightforward process than the use of thermodynamics. A major goal in chemical kinetics is to precisely know all the elementary steps that constitute the mechanism of the reaction, which entails detecting all of the intermediates along the reaction coordinate, a process that is not necessary when using thermodynamics to describe a reaction's favorability.

In this issue of *Aquatic Geochemistry*, there is a discussion paper on the batch dissolution of calcite between pH 8 and 9 by Truesdale (2015a). In this paper, he demonstrates with a plot of (Ca^{2+}) versus time that 85 % of the calcite dissolution occurs within 1 h, but dissolution continues much more slowly for days. This latter part of calcite dissolution is termed a "long tail", and it indicates a non-ideal stage for calcite dissolution. In contrast, other solids such as sodium chloride, sucrose, silica gel and gypsum show a simple exponential rise for the entire reaction. This ideal behavior can be explained using the shrinking object (SO) model with two rate constants (one for the forward dissolution reaction and a second for the back or calcite formation reaction) plus terms for the surface area of the solid and the solute concentration. In his paper, Truesdale proposes an extension of the shrinking object model for calcite using empirical kinetics or chemical templating that describes calcite dissolution using a time- or concentration-dependent function for

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apparent surface area to allow for its change by poisoning or morphology differences as the reaction proceeds.

Three comment papers follow Truesdale's discussion paper and demonstrate different ways to describe the kinetics of calcite (and other mineral) dissolution. The first comment by Icenhower (2015) discusses the limitations of transition state theory in describing the dissolution of calcite and other minerals because of the possible precipitation of metastable intermediates and surface reaction layers; thus, there is a need for additional kinetic research on the dissolution of minerals. The second comment by Turner (2015) shows that the use of Pitzer equations in the shrinking object model can lead to more accurate calcite dissolution kinetics. The third comment by Arvidson et al. (2015) discusses the determination of rate constants using the shrinking object model in conjunction with the need to know more about the molecular processes of mineral dissolution at the surface of the mineral. Truesdale (2015b) provides a final summation comment indicating that there appears to be more agreement than disagreement with his initial discussion paper.

I hope that the readership will enjoy reading these papers and understand the complexity and power of chemical kinetics. Although the geochemist's goal is to understand the exact reaction mechanism while obtaining the rate of a particular reaction along with the reaction order of each reactant in the rate law expression, it is very rare to trap the intermediates that are responsible for the exact reaction mechanism. In most cases, the intermediates can only be inferred.

References

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