

## Recent trend of reactive transport modeling of rock weathering

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The weathering of rock proceeds by the dissolution of primary minerals, the precipitation of secondary products, and the transport of materials in the pores of the rock. To quantitatively understand these processes, the analysis using the reactive transport equation is performed (reactive transport modeling). The following equation is an example of the one-dimensional reaction-transport equation:

$$p(dc/dt) = D(d^2c/dx^2) - vp(dc/dx) + Ar_0f(c)$$

where  $c$  is the solute concentration,  $t$  is the time,  $x$  is the distance,  $p$  is the porosity,  $D$  is the effective diffusion coefficient,  $v$  is the flow rate in pores,  $A$  is the surface area per unit volume of rock,  $r_0$  is the rate constant, and  $f(c)$  is the function that expresses the concentration dependence of the dissolution rate. By solving the reaction-transport equation, we can know the distributions of the solute concentration and dissolution rate in the rock, and their time variations. As the method to determine the parameters used in the calculation, for example,  $D$  can be determined by direct experimental measurement (Yokoyama and Nakashima, 2005) or by empirical equation (Archie's law). As for the reaction term, several rate laws, such as linear TST law (Aagaard and Helgeson, 1982; Lasaga, 1984), Al inhibition model (Oelkers et al., 1994), and parallel rate law (Hellmann and Tisserand, 2006), have been proposed. In the case of the reaction of quartz,  $f(c)$  is equal to  $1 - c/c_{eq}$ , where  $c_{eq}$  is the equilibrium concentration (Lasaga, 1998). By comparing the result of calculation with the actual weathering profile, we can discuss various topics including the mechanism of weathering and the reason of the discrepancy between the dissolution rates obtained in the field and in the laboratory (White and Brantley, 2003).

As some of the recent studies on reactive transport modeling, Maher et al. (2009) showed that the weathering profiles observed in soils can be reproduced by using the rate constants (based on the Al inhibition model and parallel rate law) similar to those estimated from the results of laboratory dissolution experiments, and also suggested that the precipitation of secondary products plays an important role in controlling the amount of dissolution of primary minerals. Maher (2010) proposed that weathering rate is strongly dependent on fluid residence time and flow rate. Navarre-Sitchler et al. (2011) showed that the rate of formation of the weathering rind and the distribution of the primary and secondary minerals in basalt can be explained by incorporating the time variations of  $p$ ,  $D$ , and  $A$  into the modeling. Moore et al. (2012) indicated that the average flow rate and the reactive surface area that are smaller than measured values need to be used to reproduce the weathering profile of granite by the modeling.

At present, the concentration dependences of the dissolution rates obtained at temperature higher than ambient temperature (e.g., 150 degree C) are usually directly used to analyze the reaction at ambient temperature, but its relevance is uncertain. In addition, although the precipitation rate of secondary product largely affects the result of modeling, information of the precipitation rate law of a secondary product of interest (e.g., poorly crystalline aluminosilicate) is often insufficient. Furthermore, the pores in the rock near the ground surface often become unsaturated, but little is known about the extent to which reactive surface area differs under unsaturated and saturated conditions. To resolve these problems would be important to improve the accuracy of the reactive transport modeling.

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