
Quantification of the Kinetics of Water-Rock Interactions from the Atomic to the Field Scale

/JACQUES SCHOTT

Laboratoire des Mécanismes et Transferts en Géologie (LMTG), Université de Toulouse – CNRS – Observatoire Midi-Pyrénées, 14 avenue Edouard Belin, 31400 Toulouse (France)

e-mail:

The kinetics of mineral dissolution/precipitation plays an important role in various processes occurring at the Earth surface, including continental weathering that exerts a major control on the migration of major and trace elements in the critical zone, the chemistry of rivers, the regulation of ocean and atmosphere compositions, and ultimately the climatic evolution of the Earth surface. As a result, many efforts have been recently dedicated to the quantitative description of weathering at different scales based on reactive transport modeling approaches. The accuracy of such modeling depends heavily on the robustness of kinetic models and thermodynamic and kinetic parameters used for describing mineral-water reactivity. In this presentation we focus on the quantification of the kinetics of mineral-water interactions (especially dissolution and precipitation). It is shown that the kinetics of most mineral-water reactions can be described within the framework of transition state theory (TST) that assumes that reactants have to pass an energy barrier called the activated complex to yield products. The reaction rate is proportional to the concentration of the activated complex which is assumed to be in equilibrium with the reactants. This assumption considerably simplifies the understanding and modeling of mineral dissolution kinetics by providing a direct link between rates and the thermodynamics of solution-mineral interface reactions. Building on i) the existing correlations between the thermodynamics of mineral surface and aqueous reactions and ii) mineral structure and metal-oxygen bond strength, it is shown that the contrasting kinetic behavior of minerals (oxides, silicates, carbonates, phosphates...) can be rationalized and that their dissolution/precipitation rates as a function of pH, solution composition,

chemical affinity and temperature can be predicted within the TST framework from aqueous chemistry of their constituting cations and anions. Moreover, it is shown that aqueous thermodynamics can provide accurate predictions of minerals kinetic behavior at fluids compositions and temperatures for which there is no kinetic data. This link between thermodynamics and kinetics should facilitate creation of a comprehensive kinetics data base similar to those thermodynamic data bases created by Helgeson and co-workers, enabling the real time modeling of reactive transport in natural systems.

To illustrate the potentiality of the mechanistic description of water-rock interactions in the field, a numerical model of chemical weathering in soil horizons and underlying bedrock (WITCH) has been coupled with a numerical model of water and carbon cycles (ASPECT, LPJ) and a global climate model (GENESIS) to compare observed and calculated soil profiles and water chemistries developed at different spatial and time scales. We show that the accuracy of numerical modelling of weathering (notably the soil spatial and temporal distribution of minerals) is highly dependent on a large set of parameters, among which kinetic (dissolution and precipitation rate constants, dependence of rates on chemical affinity and solution composition...) and thermodynamic parameters are essential. Water fluxes and chemical exchanges with the living and dead biomass have also a big impact on weathering profiles. Among all those critical parameters, the exact reactive surface area may be considered as a calibration parameter. It is believed that we are now getting close to a mechanistic and robust description of weathering processes in the field.