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Thermodynamic-kinetic modeling of chemical weathering of basaltic tephra on Hawaii

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Abstract

A thermodynamic-kinetic model for interactions in water-rock systems has been modified to calculate water-rock interactions during fluid flow. We used published data on chemical composition of atmospheric precipitates at Hawaii and their abundance in Kaka Falls aria, the Island of Hawaii, a level of surface runoff, age and initial composition of basaltic tephra, mineralogical zoning of laterites, to adjust such a parameter of the model as a degree of exposure of the primary mineral surfaces to aqueous solution. The goal was to obtain an approximate agreement of scales of simulated and observed mineral alterations during certain time.

Keywords: chemical thermodynamics, geochemical modeling, chemical weathering

1. Introduction

Chemical-thermodynamic modeling has significant restrictions to calculate water-rock interactions at moderate temperatures, because it does not take into account rates of chemical reactions among minerals and aqueous solutions. Earlier a thermodynamic-kinetic model was developed to describe a chemical evolution of water-rock systems over time[1,2]. It is based on a partial equilibrium principle and on the assumption that secondary minerals form during dissolution of primary minerals, which is a limiting stage of the process[3]. Rates of mineral dissolution, r_i, are individual for different minerals and depend on temperature, pH, and a degree of solution saturation. Our experience showed that the model was able to calculate correctly mineral formation and evolution of solution composition, but it is not clear, how adequately it calculates a real duration of the process in time. Here, we attempt

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to adjust a model using data on approximate duration of weathering basaltic tephra, its initial chemical and mineral composition and porosity, size of mineral grains, chemical composition and abundance of rainfall. The goal of the study was to reproduce numerically the real rate of weathering. Because parameters for mineral dissolution rates are determined, as well as a flow of water and sizes of mineral grains are specified, the only parameter to adjust is the degree of exposure of primary mineral surface area to solution. That parameter may be treated as a bulk structural property of the rock, which reflects mineral contact with aqueous solution.

2. Short description of the model

Rate of mineral dissolution is calculated for the current pH and degree of disequilibrium with respect to a dissolving mineral according to

$$r_i = [k_H(a_{H^+})^n + k_{H2O} + k_{OH}(a_{OH^-})^m] \cdot exp\left[\frac{E_a}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \cdot \left\{1 - exp\left[p\left(\frac{\Delta G}{RT}\right)^q\right]\right\}$$
(1)

In equation, the first term in square brackets describes the pH dependence of the dissolution rate[4]. The second term designates an Arrhenius-like equation that describes the temperature dependence of the rate. The third major term is used to simulate the decrease in the dissolution rate as chemical equilibrium is approached[5,6]. a_{H^+} and a_{OH-} are activities of ions H^+ and OH^-; k_H, k_{H2O}, k_{OH}, n and m – fitting parameters for various minerals. Here we used kinetic parameters from[6-8]. T_0 and T are reference and current temperatures; E_a is an apparent activation energy. ΔG is the driving force of the reaction, which reflects the degree of saturation with respect to a mineral. Coefficients p and q are adjustable parameters obtained by fitting near-equilibrium kinetic data available for some minerals.

Weathering is modelled as a series of consecutive equilibrations in aqueous solution calculated at each time step k. For each equilibrium computation, mass balance b_{jk} for every chemical element j is calculated from the chemical composition of aqueous solution at the previous step $b_{j,k-1(aq)}$ and masses of minerals Δx_{ik} to be dissolved: $b_{jk} = b_{j,k-1(aq)} + \sum \Delta x_{ik}\nu_{ji}$, where ν_{ji} is a number of stoichiometric units of jth chemical element in a formula of a mineral i. $\Delta x_{ik} = S_{ik}^{ex} r_{ik} \Delta t_k$, where S_{ik}^{ex} is the exposed surface area of the ith mineral (m^2), proportional to geometric surface area via some coefficient: $S^{ex} = Fs_i \cdot S_i^g$, Δt_k is duration of a time step (s), r_{ik} is a current rate of dissolution ($mole \cdot m^2 \cdot s^{-1}$). Minerals, deposited at previous time steps, are considered primary ones and can be dissolved if they are not in equilibrium with the solution. The duration of each time step was determined numerically from a specified molar amount of the fastest dissolving mineral. Therefore similar masses were introduced into solution during each time step to prevent significant change of pH. Geometric surface areas of minerals are calculated from their volumes in the rock and initial grain sizes, and further as they change in time due to dissolution or deposition.

Calculation of interactions during flow supposes that every exiting portion of solution replaces the previous portion in the underlying layer. Hence, there is a constant short duration of time steps for all layers and a significant increase of time of computation.

3. Input data

Here the normalized mineral composition of fresh basaltic tephra of the Island of Hawaii[9] (Table 2, Column 1) is as follows (mole per kg): olivine ($Fa_{0.5}Fo_{0.5}$) 0.232; clinopyroxene ($Di_{0.5}He_{0.5}$) 1.834; orthopyroxene ($Mg_{0.75}Fe_{0.25}$) 1.162; plagioclase (Oligoclase) 1.5; ilmenite 0.32; magnetite 0.103. A grain size for all minerals is 0.001 mm. Porosity of tephra is 36%. The work[9] also describes chemical and mineral alteration during weathering, compositions and pH of pore waters of variously altered tephra. The age of basalts and thus time of weathering do not exceed 10000 years.

Based on a paper[10] on chemical composition of cloud water over Hawaii, we took a model salt composition of atmospheric precipitates (Na^+ $1 \cdot 10^{-4}$; Cl^- 2 10^{-4}; SO_4^{2-} 1 10^{-5} mole/kg H_2O; pH=5.68). Average rainfall in the area of Kaka Falls, according to[9] is accepted as 600 cm/year. Surface runoff aggregates 40%.

We took a 11-component system: O, H, Mg, Ca, Al, C, Si, Ti, Na, Cl, Fe; 35 potential minerals, 48 aqueous species. The system was open with respect to atmospheric oxygen and carbon dioxide. Temperature was taken as 298.15 K. The proportions of rainfall and surface runoff, and basaltic tephra porosity and density suppose that at a