

# Replacement reactions during weathering: macrokinetic approach

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From the physico-chemical standpoint the process of weathering can be treated as a sequence of reactions resulting in replacement of one set of minerals by others during water-rock interaction. On the other hand, weathering may be considered as a long-term process of transformation of large volumes of rocks, and attempts to make paleoreconstructions of this process give rise to development of phenomenological models with sets of equations for mass transfer and water-rock interaction. The physico-chemical mechanism of interaction is usually written into these models by source/sink type equations, which express, as a rule, empirical regularities of the kinetics of initial steps of the process most extensively studied experimentally.

In this work the macrokinetic approach is used to examine the process of weathering, and it is considered as a combination of steps of different origin, including not only chemical acts of interaction proper, but also transport stages. In doing this, the relationships between the rates of all particular steps and their change with the progress of reactions is solved (Rosovsky, 1980).

A characteristic feature of aluminosilicate weathering processes are reactions precipitating hydroxides (mainly Al, Fe and Mn) 'very quickly' after water first contacts a fresh rock surface. The reactions, including at least one solid reagent and solid reaction product (so-called topochemical reaction), are characterised by a narrow reaction zone which is usually considered as a surface of reaction (Rosovsky, 1980).

The change of the topochemical reaction rate with time is noteworthy. In the beginning, the rate is low (step of the nucleation), it then increases (surface area of nuclei grow up), passes through the maximum (separate nuclei merge together), and then decreases to values which vary only slightly with time (as the interface primary mineral-replacing mineral moves inward to the bulk of the primary mineral). With displacement of the reaction zone inward, every host mineral grain can change the kinetic regime of reaction (rate-limiting step) even on retention of constant concentration, thermodynamic and hydrodynamic conditions, and the macrokinetic process may be very intricate.

## Rate of mass transfer through the layer of secondary minerals

It seems that in studies of the kinetics of aluminosilicate dissolution, the majority of investigators try to avoid the problem of the influence of the precipitation of secondary minerals on the overall rate process. With a view to estimating the role of the layer of precipitates and its effect on diffusion, I present the following simple model.

Let us assume that the surface of the primary mineral reacting with the solution is already covered by a continuous layer of the solid reaction product. The flux of components (reagents) through this layer we can express as:

$$J_1 = \frac{D^*}{L} \cdot (C_p - C_s) \cdot S_1 \quad (1)$$

where  $D^*$  is the effective coefficient of the diffusion through the layer of the solid reaction product;  $L$  is the thickness of the solid reaction product layer;  $C_p$  is the concentration of the component on the surface of the solid reaction product;  $C_s$  is the concentration of the component on the reaction surface and  $S_1$  is the surface of the cross-section of the solid reaction product layer, which is perpendicular to the concentration gradient.

The flux of components on the reaction surface, assuming for simplification a first order surface irreversible reaction, is as follows:

$$J_2 = k \cdot C_s \cdot S_2 \quad (2)$$

where:  $k$  is the rate constant of the surface reaction and  $S_2$  is the reaction surface area.

Assuming a steady state, we consider that the fluxes of dissolved components from the bulk of the solution towards the surface of the reaction product layer, through this layer and on the surface of reaction are equal. Thus, neglecting the diffusion resistance of the dilute solution and assuming for simplification  $S_1 = S_2 = S$ , we can write

$$\frac{dm}{dt} = \frac{D^*}{L} \cdot (C - C_s) \cdot S = k \cdot C_s \cdot S \quad (3)$$

where  $C$  is the bulk concentration of the

component in the solution and  $m$  is the weight of the solid reaction product at the moment of time  $t$ .

From equation (3) 'driving forces' of the mass transfer are :

$$C - C_s = \frac{dm}{dt} \cdot \frac{L}{D^* S} \quad (4)$$

$$C_s = \frac{dm}{dt} \cdot \frac{1}{kS} \quad (5)$$

Summarising we obtain:

$$C = \frac{1}{S} \cdot \frac{dm}{dt} \cdot \left( \frac{L}{D^*} + \frac{1}{k} \right) \quad (6)$$

The change in weight of the solid reaction product is:

$$dm = \rho \cdot \zeta \cdot S \cdot dL \quad (7)$$

Here  $\rho$  is the density of the reaction product and  $\zeta$  is the stoichiometric coefficient.

After substituting equation (7) in (6) and integration we have:

$$\frac{L^2}{2D^*} + \frac{L}{k} = \frac{C \cdot t}{\zeta} \quad (8)$$

If we assume that surface reaction is relatively fast after reaching the overall rate maximum, we can neglect the second term of equation (8). In this case we find so-called parabolic reaction law, which is typical for the diffusion-controlled range of the topochemical reaction:

$$L = k^* \cdot (C \cdot t)^{1/2} \quad (9)$$

where

$$k^* = \left( \frac{2D^*}{\rho \cdot \zeta} \right)^{1/2} \quad (10)$$

From equation (10) we can see that the rate of the replacement reaction in this kinetic range is dependent upon the effective coefficient of the Diffusion  $D^*$  through the layer of the solid reaction product. This means that the rate of the replacement may be determined, to a large extent, by the structure of this layer.

#### Pseudomorphic replacement and diffusion

The structure of the secondary mineral aggregates which determine their permeability for dissolved reactants and reaction products, depends on various factors of both thermodynamic and kinetic origin. Preservation of the overall mineral volume (volume including porosity) during pseudomorphic replacement and the formation of considerable (micro)porosity of the weathering products at the same time, gives a situation where

'volume-for-volume' replacement is not obeyed (Dobrovolsky and Lyalko, 1978). Extensive replacement by mechanisms close to pseudomorphic (Dobrovolsky, 1987; Merino et al., 1993) is only possible when the molar volume of secondary minerals is less than the primary one (Dobrovolsky, 1984).

The rate-controlling role of the diffusion through the layer of secondary minerals is still a controversial problem and values of effective coefficients of the diffusion through the fine-grained mineral aggregates range widely (Dobrovolsky and Sukach, 1977; Petrovic, 1976; Busenberg and Clemency, 1976). The thickness of a certain structure layer (defining the value of  $D^*$ ) whose resistance to diffusion is sufficient that it should start to control the overall rate of the replacement process may be estimated. Calculations for potassium feldspar and nepheline dissolution, indicate that diffusion through the layer of secondary mineral will be rate controlling when that layer is respectively 0.4 cm and 0.002 cm thick.

It is concluded that the processes of metasomatic replacement, where kinetics is controlled by diffusion through the layer of precipitates, should be widespread in real conditions of the Earth's Crust. Production of secondary minerals structures is a formidable problem, particularly considering the change of precipitate layer structure with time (for example, ageing of colloid phases, recrystallisation etc.); so determination of effective coefficients of diffusion is possibly one of the most difficult problems when modelling the dynamics of natural replacement processes.

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