

EXPERIMENTAL AND MATHEMATICAL MODELING OF REACTIONS KINETICS OF MINERALS TRANSFORMATION

Alekseyev V.A., Medvedeva L.S., Bannykh L.N. (GEOKHI RAS)

alekseyev@geokhi.ru; phone: (095) 137-58-37

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At 300°C and pH 9 experiments have been performed in the systems albite + analcime + 0.1 *m* NaHCO₃ and albite + sanidine + 0.1 *m* KHCO₃ in isolated platinum capsules by quenched method. Crushed minerals were preliminary treated with fresh portions of solutions under the same conditions to dissolve fine particles and surface defects.

In the system albite + analcime + 0.1 *m* NaHCO₃ (fig. 1) albite was dissolving for all time. Analcime at first was dissolving and after 3 hours was precipitating. These reactions were modeled by solving the system of equation:

$$dm_{Na}/dt = -(r_{Ab} - r_{Anl})/M, \quad (1)$$

$$dm_{Al}/dt = -(r_{Ab} - r_{Anl})/M, \quad (2)$$

$$dm_{Si}/dt = -(3r_{Ab} - 2r_{Anl})/M \quad (3)$$

Here m_{Na} , m_{Al} , m_{Si} are molal concentrations of elements in solution, t is time, M is mass of solution, r_{Ab} and r_{Anl} are rates of albite dissolution and analcime precipitation which have general expression:

$$r = -kS[1 - (Q/K)^\sigma], \quad (4)$$

where k is rate constant, S is surface area of mineral, Q and K are activity product and equilibrium constant of reaction, σ is coefficient. The results of modeling are consistent with the experimental data only if different values of kS for reactions of analcime dissolution and precipitation are used in the rate equation (4) (fig. 1). This means violating the principal of microscopic reversibility of the reactions.

In the system albite + sanidine + 0.1 *m* KHCO₃ (fig. 2) albite was dissolving and sanidine was precipitating. However $m_{Al} < m_{Si}/3$ and this fact contradicts the reactions stoichiometry. Values of x in albite formula $Na_{1+x}Al_{1+x}Si_{3-x}O_8$ were calculated from solution composition postulating that sanidine was precipitated stoichiometrically. These data were approximated by equation:

$$x = 0.1 - 0.11[1 - (Q/K)^{6.7}] \quad (5)$$

The calculations have been shown that small deviations from stoichiometry in dissolving albite (~1%) increase in solution as much as overall amounts of elements passed through solution exceed their concentration in solution

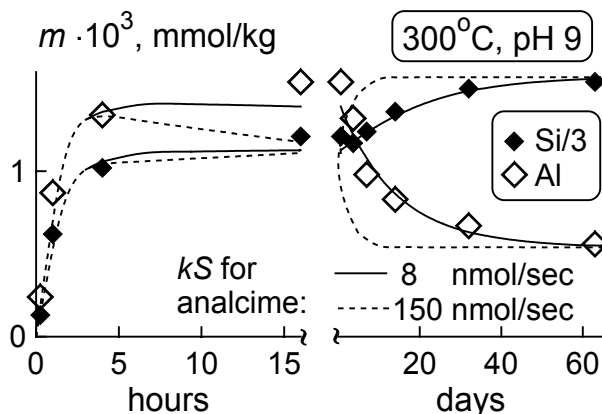


Fig. 1. Concentrations of elements in solution versus time in the system albite + analcime + 0.1 *m* NaHCO₃. Symbols are experimental data, lines are results of calculations according to equations (1) – (4) with $\sigma = 1$, $K_{Ab} = 8.0 \times 10^{-13}$, $K_{Anl} = 1.8 \times 10^{-10}$.

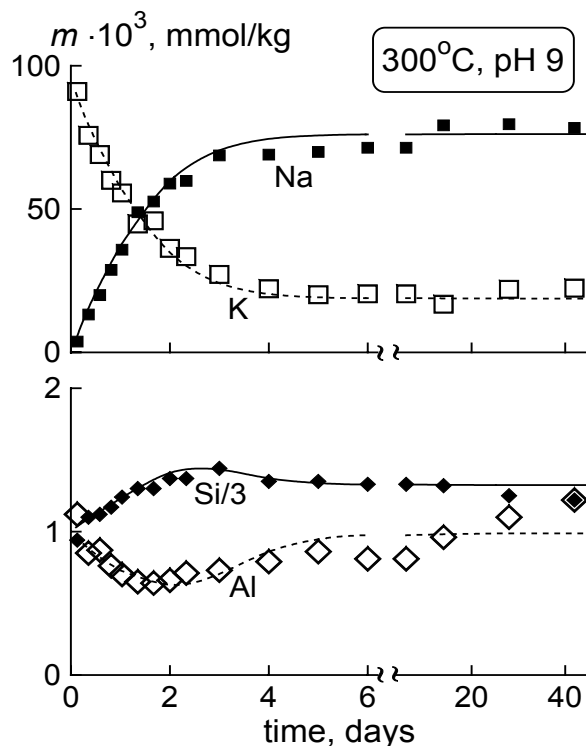


Fig. 2. Concentrations of elements in solution versus time in the system albite + sanidine + 0.1 *m* KHCO₃. Symbols are experimental data, lines are results of calculations according to equations (4) – (9).

Parameters of equation (4) are shown in fig. 3. (about 2 orders of magnitude).

The rates of albite dissolution and sanidine precipitation were calculated from the slopes of kinetic curves in coordinates of concentration versus time. The data were approximated by the same rate equation (fig. 3) proving microscopic reversibility of the reactions and in particular identity of active sites of primary mineral dissolution and secondary mineral precipitation. To model the substitution reaction of albite to sanidine the following system of equations was solved:

$$dm_K/dt = -r_{San}, \quad (6)$$

$$dm_{Na}/dt = -r_{Ab}(1+x), \quad (7)$$

$$dm_{Al}/dt = -(r_{Ab}(1+x) + r_{San}), \quad (8)$$

$$dm_{Si}/dt = -(r_{Ab}(3-x) + 3r_{San}), \quad (9)$$

where x is determined by expression (5) and rates of albite dissolution (r_{Ab}) and sanidine precipitation (r_{San}) are determined by equation (4) with coefficients shown in fig. 3. The results of modeling are in good agreement with the experimental data (fig. 2).

Shapes of kinetic curves are different depending on what secondary mineral is precipitating (fig. 4). The explanation is that in case A dissolution sites of primary mineral and precipitation sites of secondary mineral are different but in case B they are the same. As a result in case A these two processes do not retard each other but in case B precipitation of secondary mineral prevent from dissolution of primary mineral. This hypothesis was proved by series of kinetic particularities of transformation reaction of albite to sanidine. One of them was stated in the description of fig. 3. The others are in the paper [1]. They concern neighborhood of sites of primary mineral dissolution and secondary mineral precipitation, presence of induction period between congruent and incongruent stages of albite dissolution.

The methodical approach used in this work may be useful for kinetic description of other substitution reactions of minerals.

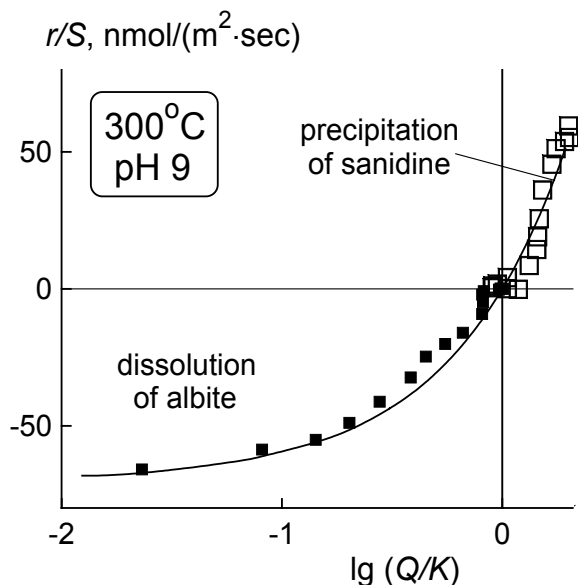


Fig. 3. Specific rates of albite dissolution and sanidine precipitation (r/S) versus saturation state of solution (Q/K). Symbols are experimental data, line is a result of calculations according to equation (4) with $k = 70 \text{ nmol m}^{-2} \text{ sec}^{-1}$, $S = 7.7 \text{ m}^2$, $\sigma = 0.8$, $K_{Ab} = 6.6 \times 10^{-13}$, $K_{San} = 1.6 \times 10^{-13}$.

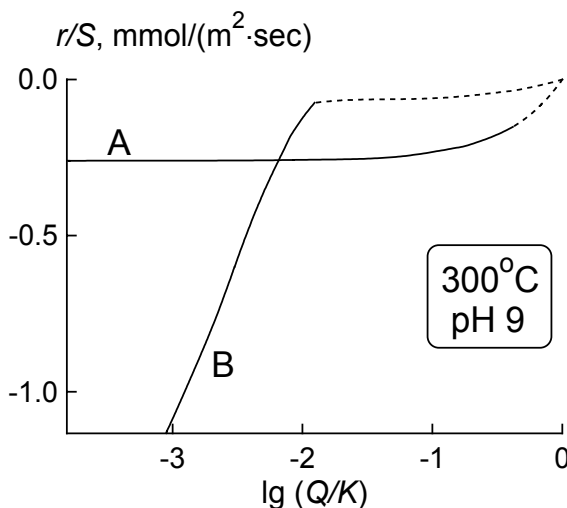


Fig. 4. Specific rates of albite dissolution versus saturation state of solution. Solid parts of curves correspond to congruent dissolution. Dashed parts correspond to incongruent dissolution with formation of analcime (A) or sanidine (B) as secondary mineral. Solutions (0.1 m) are: NaHCO_3 (A) и KHCO_3 (B). Data of figures 1, 3, and paper [1] are summarized.

Reference:

1. *Alekseyev V.A., Medvedeva L.S., Prisyagina N.I. et al. Geochim. et cosmochim. acta. 1997. V. 61. № 6. P. 1125 – 1142.*

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